

# Occupational Health Guideline for Petroleum Distillates (Naphtha)

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula:  $C_6H_{14}$  —  $C_7H_{16}$  —  $C_{10}H_{22}$
- Synonyms: Petroleum naphtha; aliphatic petroleum naphtha; petroleum ether (95 to 115 C); naphtha, petroleum
- Appearance and odor: Colorless liquid with an odor like gasoline and kerosene.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for petroleum distillates is 500 parts of petroleum distillates per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2000 milligrams of petroleum distillates per cubic meter of air ( $mg/m^3$ ). NIOSH has recommended that the permissible exposure limit be reduced to 350  $mg/m^3$  averaged over a work shift of up to 10 hours per day, 40 hours per week.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Petroleum distillates can affect the body if they are inhaled, come in contact with the eyes or skin, or are swallowed.

### • Effects of overexposure

1. *Short-term Exposure:* Overexposure to petroleum distillates may cause dizziness, drowsiness, headache, and nausea. They may also cause irritation of the eyes, throat, and skin.

2. *Long-term Exposure:* Prolonged overexposure may cause drying and cracking of the skin.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to petroleum distillates.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to petroleum distillates at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from petroleum distillates exposure.

—Skin disease: Petroleum distillates are skin defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of petroleum distillates might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Although petroleum distillates are not known as liver toxins in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although petroleum distillates are not known as kidney toxins in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

### • Summary of toxicology

The vapors of petroleum distillates are mild narcotics and mucous membrane irritants. There have been few toxicologic studies, either on animals or man. While 4000 to 7000 ppm are tolerated for 1 hour by human subjects, symptoms of narcosis, such as dizziness and drowsiness, occur at those concentrations. Continuing

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

exposure may produce signs of inebriation, followed by headache or nausea. Exposure at 10,000 to 20,000 ppm is regarded as immediately hazardous to life. The higher boiling fractions may produce irritation of the eyes, nose, and throat in addition to symptoms of mild narcosis. The liquid is a defatting agent, and repeated or prolonged skin contact results in drying and cracking of the skin. No chronic systemic effects have been reported from widespread industrial use. If benzene is present in the distillate, however, the hazard of both acute and chronic poisoning is increased; the presence of elevated phenol in the urine is indicative of benzene exposure.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 100 (approximately)
2. Boiling point (760 mm Hg): 30 to 127 C (86 to 260 F)
3. Specific gravity (water = 1): 0.74
4. Vapor density (air = 1 at boiling point of petroleum distillates): 3.4 (approximately)
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): 40 mm Hg (approximately)
7. Solubility in water, g/100 g water at 20 C (68 F): 0.04 (approximately)
8. Evaporation rate (butyl acetate = 1): 10 (approximately)

### • Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving petroleum distillates.
4. Special precautions: Petroleum distillates will attack some forms of plastics, rubber, and coatings.

### • Flammability

1. Flash point: -40 to 20 C (-40 to 68 F) (closed cup)
2. Autoignition temperature: 232 to 260 C (450 to 500 F)
3. Flammable limits in air, % by volume: Lower: 1; Upper: 6
4. Extinguishant: Foam, carbon dioxide, dry chemical

### • Warning properties

1. Odor Threshold: The odor thresholds of the main constituents of petroleum naphtha (i. e., heptane, octane, pentane, etc.) are below the individual permissible exposure limits.
2. Eye Irritation Level: According to Gafafer, the naphthas irritate the conjunctiva. The American Petroleum Institute states that irritation of the conjunctiva may occur "when the eyes are exposed to high vapor concentrations (of petroleum naphtha) in air. The irritation is mild and transitory." No quantitative information is available concerning the threshold of eye irritation,

however.

3. Evaluation of Warning Properties: Since the odor of each of the main constituents of petroleum naphtha is detectable at concentrations below the respective permissible exposure limits, petroleum naphtha is treated as a material with adequate warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

### • General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Method

Sampling and analyses may be performed by collection of petroleum distillates vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure petroleum distillates may be used. An analytical method for petroleum distillates is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid petroleum distillates.

- Clothing wet with liquid petroleum distillates should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of petroleum distillates from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the petroleum distillates, the person performing the operation should be informed of petroleum distillates' hazardous properties.
- Any clothing which becomes wet with liquid petroleum distillates should be removed immediately and not reworn until the petroleum distillates are removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid petroleum distillates may contact the eyes.

## SANITATION

- Skin that becomes wet with liquid petroleum distillates should be promptly washed or showered with soap or mild detergent and water to remove any petroleum distillates.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to petroleum distillates may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during degreasing operations	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as solvents in rubber industry during manufacture of water-proof cloth, shoe adhesives, and rubber tires	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as extractants; use in preparation of paint, varnish, and lacquer as solvents, diluents, or thinners; use as solvents in pesticides	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during dry cleaning operations	General dilution ventilation; local exhaust ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If petroleum distillates get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation persists after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

### • Skin Exposure

If petroleum distillates get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If petroleum distillates soak through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of petroleum distillates, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

If petroleum distillates have been swallowed, do not induce vomiting. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If petroleum distillates are spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Petroleum distillates should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

Petroleum distillates may be disposed of by atomizing in a suitable combustion chamber.

## REFERENCES

- American Industrial Hygiene Association: "Petroleum Naphtha," *Hygienic Guide Series*, Detroit, Michigan, 1969.
- American Petroleum Institute: "Petroleum Distillates," *API Toxicological Reviews*, New York.
- Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Gafafer, W. M. (ed.): "Occupational Diseases: A Guide to Their Recognition," U.S. Public Health Service Publication No. 1097, 1964.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Pagnotto, L. D., et al.: "Industrial Benzene Exposure from Petroleum Naphtha: I. Rubber Coating Industry," *American Industrial Hygiene Association Journal*, 22:417-421, 1961.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

## RESPIRATORY PROTECTION FOR PETROLEUM DISTILLATES (NAPHTHA)

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
5000 ppm or less	A gas mask with a chin-style organic vapor canister.
10,000 ppm or less	A gas mask with a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

\*Only NIOSH-approved or MSHA-approved equipment should be used.



# The North Carolina Toxic Substances Management Guide

## ARSENIC

### Executive Summary

CAS NUMBER: 07440-38-2

Arsenic is a silver-gray or tin-white, brittle element possessing both metallic and non-metallic (metalloid) properties. Arsenic exists in the +5, +3, 0, and -3 oxidation sites, and its compounds may be classified according to the oxidation state and according to whether arsenic is in the organic or inorganic form. Arsenic is prepared commercially by the reduction of arsenic trioxide or by direct smelting of the minerals arsenopyrite ( $\text{FeAsS}$ ) and loelligite ( $\text{FeAs}_2$ ). Arsenic trioxide is the most common form of commercially prepared arsenic, although there are about 50 arsenic compounds produced in the U.S. Most of the arsenic used in the U.S. is imported from Sweden, with 1978 imports estimated at 335,000 kg. Arsenic and its compounds are used in the manufacturing of glass, cloth and semiconductors, as fungicides and wood preservatives, in metal hardening and in various agricultural and veterinary applications. Federal regulations require the reporting of spills over 5,000 pounds for the following arsenic compounds: arsenic disulfide, arsenic pentoxide, arsenic trichloride, arsenic trioxide, and arsenic trisulfide. North Carolina requires the reporting of all spills of these compounds if they occur near water.

#### Health Effects

**ACUTE.** The acute toxic effects of arsenic usually follow the ingestion of inorganic arsenic compounds. Signs and symptoms may vary according to the amount and form involved, but the major characteristics of acute poisoning include profound gastrointestinal damage and cardiac abnormalities, shock and death.

**CARCINOGENICITY.** There is substantial evidence that atmospheric arsenic is a human carcinogen. Epidemiological studies have revealed a marked elevation in respiratory cancer rates for workers exposed to lead arsenate and calcium arsenate.

**MUTAGENICITY.** Existing data are inconclusive with regard to arsenic's ability to cause mutations, although arsenic compounds do induce chromosomal aberrations in mammalian cells.

**TERATOGENICITY AND EMBRYOTOXICITY.** Sodium arsenate has been found to cause birth defects in chicks and mice.

**CHRONIC.** Inhalation of inorganic arsenic compounds is the most common cause of chronic arsenic poisoning. Symptoms include weakness, loss of appetite, nausea and other gastrointestinal disturbances, most of which subside when exposure is halted.

#### Occupational Health Regulations (for elemental arsenic)

**ACGIH:** The Threshold Limit Value (TLV) for workroom air is 200  $\mu\text{g}/\text{cu m}$  as a time-weighted average.

**NIOSH:** The standard for workroom air is 2  $\mu\text{g}/\text{cu m}$  (inorganic arsenic) as a time-weighted average.

**OSHA:** The standard for workroom air is 500  $\mu\text{g}/\text{cu m}$  as a time-weighted average.

#### Routes of Human Exposure

A partial list of occupations in which exposure may occur includes:

Alloy makers	Lead shot makers
Aniline color makers	Lead smelters
Arsenic workers	Leather workers
Babbitt metal workers	Painters
Brass makers	Paint makers
Bronze makers	Petroleum refinery workers
Ceramic enamel makers	Pigment makers
Ceramic smelters	Printing ink workers
Copper smelters	Rodenticide makers
Drug makers	Semiconductor compound makers
Dye makers	Silver refiners
Enamels	Taxidermists
Fireworks makers	Textile printers
Gold refiners	Tree sprayers
Herbicide makers	Type metal workers
Hide preservers	Water weed controllers
Insecticide makers	Weed sprayers

**AMBIENT.** Arsenic is ubiquitous in the environment, usually in very low concentrations. Elevated levels occur as a result of runoff, drainage or contamination from arsenic-rich soils or rocks. Ambient exposure is not considered to be a significant health threat to humans.

**CONSUMER.** Arsenic can be present in small amounts in food as a result of contamination or as a residue of lead or calcium arsenate used as insecticides, particularly on potatoes and fruit. The estimated average daily consumption of arsenic from food is calculated to be 0.15-0.40 mg/person.

#### Environmental Significance

Arsenic accumulates in sediments, animals and plants at lower trophic levels. Marine organisms have the highest concentrations of arsenic found in living organisms. It is mobile in the aquatic environment to the extent that it is metabolized by a number of organisms to organic arsenicals. For freshwater aquatic life the concentration of total recoverable trivalent inorganic arsenic should not exceed 440  $\mu\text{g}/\text{cu m}$  at any time.

#### Recommended Reviews

Committee on Medical and Biologic Effects of Environmental Pollutants, Arsenic. National Academy of Sciences, Washington, DC 1977

#### Technical and Microelectronic Analysis, Task II: Arsenic and Its Compounds.

Final Report (1976), EPA 560/6-76-010.

# FIRST AID AND EMERGENCY RESPONSE INFORMATION

## ARSENIC

First Aid (U.S. DOT Emergency Response Guidebook, 1980)

	Arsine	Arsenic and Arsenic Compounds
Eyes:	Flush eyes with running water for at least 15 minutes, lifting upper and lower lids occasionally.	Flush with running water for 15 minutes, lifting upper and lower lids occasionally.
Inhalation	Seek immediate medical attention. Move victim to fresh air. Give artificial respiration if victim has stopped breathing. Give oxygen if breathing is difficult.	Same as for Arsenic. Keep victim quiet and maintain normal body temperature.
Ingestion:		Give large amounts of water followed by milk. Do not induce vomiting. Seek immediate medical attention.
Skin:	Remove and isolate contaminated clothing and shoes. Wash exposed area with soap or mild detergent. If irritation persists, seek medical attention.	Same as for Arsenic.

Spills and Leaks (U.S. DOT Emergency Response Guidebook, 1980)

Arsine	Arsenic and Arsenic Compounds
Isolate hazard area and deny entry. Evacuate area endangered by gas. Stay upwind and keep out of low areas. Wear positive pressure breathing apparatus and full protective clothing. Isolate for ½ mile in all directions if tankcar is involved in fire. No flares, smoking or flames in hazard area. Stop leak if it can be done without risk. Use water spray to reduce vapors but do not put water on leak area.	Isolate hazard area and deny entry. Stay upwind and keep out of low areas. Wear positive pressure breathing apparatus and special protective clothing. Do not touch spilled material. Stop leak if it can be done without risk. Use water spray to reduce vapors.
	SMALL SPILLS: Take up with sand or other non-

Spills and Leaks (Continued)

combustible, absorbent material, then flush area with water.  
SMALL DRY SPILLS: Shovel into dry containers and cover; move containers; then flush area with water.  
LARGE SPILLS: Dike far ahead of spill for later disposal.

Fire and Explosion Information

Arsine	Arsenic and Arsenic Compounds
Extremely flammable. May be ignited by heat, sparks and flames. Flammable vapor may spread away from spill. Container may explode in heat of fire. Vapor explosion hazard indoors, outdoors and in sewers. Let burn unless fire can be stopped immediately.	Some of these materials may burn but do not ignite readily. Cylinder may explode in heat of fire. Move container from fire area if it can be done without risk. Fight fire from maximum safe distance.

SMALL FIRES: Dry chemical, CO<sub>2</sub>, water spray or foam.

LARGE FIRES: Water spray, fog or foam

Move container from fire area if it can be done without risk. Stay away from the ends of tanks and withdraw immediately in case of rising sound from venting safety device or discoloration of tank.

Reactivity

MATERIAL TO AVOID (for Arsenic): Strong oxidizers, chloride and nitric acid.

Protective Equipment

ARSENIC: For levels up to 0.5 ppm, wear a supplied-air respirator or a self-contained breathing apparatus. For levels up to 2.5 ppm, wear the above with a full facepiece. For levels up to 6 ppm, wear a supplied-air respirator operating in the positive demand, positive pressure or continuous flow mode. For escape from a contaminated area, wear a gas mask or a self-contained breathing apparatus.

ARSENIC AND ARSENIC COMPOUNDS: At levels up to 50 mg/cu m, wear a supplied-air respirator or a self-contained breathing apparatus with full facepiece. For levels up to 100 mg/cu m, wear the above operating in positive demand, positive-pressure or continuous flow mode. For escape from a contaminated area, wear a self-contained breathing apparatus.

## ARSENIC

## Profile

## Chemical Identification

## Alternative Names:

Chemical Name	Oxidation States	Formula	CAS Number
Arsenic	0	As	07440-38-2
Arsenic-75			
Arsenic Black			
Arsenic Pentoxide	+5	As <sub>2</sub> O <sub>5</sub>	1303-28-3
Arsenic Trioxide	+3	As <sub>2</sub> O <sub>3</sub>	1327-53-2
Arsenic Sulfide	+3	As <sub>2</sub> S <sub>3</sub>	1303-33-9
Arsanilic Acid			
Organometallic Arsenic		C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> AsO(OH) <sub>2</sub>	98-50-0
Arsine	-3	AsH <sub>3</sub>	7784-42-1
Calcium Arsenate	+5	Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	7778-44-1
Dimethylarsinic Acid			
Organometallic Arsenic		(CH <sub>3</sub> ) <sub>2</sub> AsO(OH)	0075-60-5
Lead Arsenate	+5	PbHAsO <sub>4</sub>	7645-25-2
Sodium Arsenate	+5	Na <sub>3</sub> AsO <sub>4</sub>	7631-89-2
Sodium Arsenite	+3	NaAsO <sub>2</sub>	7784-46-5
Arsenic Trichloride	+3	AsCl <sub>3</sub>	7784-34-1

Chemical Abstract Services (CAS) Registry  
Number: 07440-38-2

Registry of Toxic Effects of Chemical Substances  
(RTECS) Number: CG 0525000

Hazardous Materials Table Identification  
Number: UN 1561

Atomic Weight: 74.92

Atomic Symbol: As

Classification: An elemental metalloid

Description: A silver-gray or tin-white, brittle, crystalline, metallic-looking substance

Uses: Glass manufacturing, alloying agent, herbicide, insecticide, electronics and metallurgy

Chemical/Physical Data

Boiling point: 613°C  
Melting point: 817°C  
Density: 5.727 at 14°C  
Solubility in water: insoluble in water, soluble in nitric acid

## HUMAN TOXICITY

Arsenical compounds differ widely in their toxicity. Generally, the trivalent species of inorganic arsenic are substantially more toxic than

pentavalent compounds. Inorganic compounds are much more toxic than organic species, some of which are essentially nontoxic. Most toxic of all species is arsine and its methyl derivatives. Because of its virtual insolubility in water, and hence in body fluids, elemental arsenic exhibits low toxicity in humans. All arsenicals, with the exception of arsine, disturb cell metabolism through the inhibition of sulfhydryl enzyme systems. Arsine combines with hemoglobin to form a powerful hemolytic poison.

The acute toxic effects of arsenic usually follow the ingestion of inorganic arsenical compounds, and are the result of severe inflammation of the mucous membranes and increased permeability of the blood capillaries. Although signs and symptoms vary in degree and timing according to the amount and form involved, the major characteristics of acute poisoning are profound gastrointestinal damage and cardiac abnormalities. With sufficiently high doses, shock may develop due to severe fluid losses, and death may follow within 24 hours. Survival of acute effects may be followed by an exfoliative dermatitis and peripheral neuritis.

Trivalent arsenic compounds are corrosive to the skin, and prolonged contact may result in a local erythema (redness) and blistering. Moist mucous membranes are most sensitive to the irritant action. Perforations of the nasal septum may occur as a result of exposure to arsenic dust. Arsenic trioxide and pentoxide are capable of producing skin sensitization and contact dermatitis.

Inhalation of inorganic arsenic compounds is the most common cause of chronic arsenic poisoning in the industrial setting. Symptoms include weakness, loss of appetite, nausea and other gastrointestinal disturbances, most of which subside when exposure is halted. Hyperpigmentation of the skin and peripheral neuropathy may ultimately occur (IARC, 1980, EPA, WQC, 1980).

The probable oral lethal dose for humans is 5-50 mg/kg, between seven drops and one teaspoonful for a 170 kg (150 lb.) man (TDB, 1982).

Arsine and its methyl derivatives are the most highly toxic of all arsenical compounds. Inhalation of arsine concentrations of 25 ppm for 30 minutes can be fatal. The maximum level of arsine at which one could escape within 30 minutes without any escape-impairing symptoms or irreversible effects is suggested to be 6 ppm (NIOSH, 1978).

Carcinogenicity

U.S. EPA,  
CAG, 1980

There is substantial evidence that atmospheric arsenic is a human carcinogen. Workers engaged in the production of insecticides

containing lead arsenate and calcium arsenate showed a marked elevation in respiratory cancer rates based upon a retrospective proportionate mortality study.

IARC, 1979 Positive for humans.

#### Mutagenicity

U.S. EPA, CAG, 1980 The evidence that arsenic compounds cause mutations and allied effects in bacteria is inconclusive. However, arsenic compounds induce chromosomal aberrations and morphological transformation in mammalian cells (IARC, 1980).

#### Teratogenicity and Embryotoxicity

Sodium arsenate has been found to cause birth defects in chicks and mice (CAG, 1980).

#### ANIMAL TOXICITY

Arsenic poisoning produces intense abdominal pain, a staggering gait, extreme weakness, trembling, salivation, vomiting, diarrhea, a normal to sub-normal temperature and collapse. It is a potent capillary poison, causing shock and circulatory failure (Waldron, 1980).

#### Acute Toxicity

Results of lethal studies in several species are listed below (TDB, 1982):

Route	Species	Lethal Dose or Lethal Concentration
<u>Oral</u>		
As <sub>2</sub> O <sub>5</sub>	Rat	8 mg/kg, LD50
	Mice	55 mg/kg, LD50
C <sub>2</sub> H <sub>7</sub> AsO <sub>2</sub>	Rat	700 mg/kg, LD50
As <sub>2</sub> S <sub>3</sub>	Rat	298 mg/kg, LD50
	Mice	794 mg/kg, LD50
NaAsO <sub>2</sub>	Rat	41 mg/kg, LD50
C <sub>2</sub> H <sub>7</sub> AsNO <sub>3</sub>	Rat	216 mg/kg, LD50
PbHAsO <sub>4</sub>	Rat	100 mg/kg, LD50
<u>Inhalation</u>		
AsH <sub>3</sub>	Rat	300 mg/cu m/15 min, LCLo
	Dog	400 mg/cu m/15 min, LCLo
	Monkey	70 mg/cu m/15 min, LCLo
AsCl <sub>3</sub>	Mice	338 ppm/10 min, LCLo
	Cat	100 mg/cu m/1 hour, LCLo
<u>Cutaneous</u>		
NaAsO <sub>2</sub>	Rat	150 mg/kg, LD50

#### Chronic Toxicity

Route	Species	Dose/Effect
Oral (As)	Mice	120 mg/kg (pregnancy); teratogenic effect

Growth depression, chronic hepatitis and cirrhosis of the liver were noticed in rats whose diets contained 300 ppm Arsenic (Luckey, 1978).

#### Aquatic Toxicity

For freshwater aquatic life the concentration of total recoverable trivalent inorganic arsenic should not exceed 400 µg/l at any time. Short-term effects on embryos and larvae of aquatic vertebrate species have been shown to occur at concentrations as low as 40 µg/l.

The available data for total recoverable trivalent inorganic arsenic indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 508 µg/l. No data are available concerning the chronic toxicity of trivalent inorganic arsenic to sensitive saltwater aquatic life.

#### ENVIRONMENTAL DATA

##### Air

Arsenic in trace amounts (ppb) may be present normally in the air at various times. In areas remove from man-related contamination, arsenic concentrations in the air are less than 0.02 µg/cu m, whereas in urban areas they vary from less than 0.01 µg/cu m to 0.16 µg/cu m. Physical removal from the atmosphere may occur as a result of rainfall; photolysis is not an important process in determining the fate of arsenic in the air (Waldron, 1980; Callahan, 1979).

##### Water

Almost all natural waters contain arsenic. Seawater has an average of 3-4 parts per billion; this concentration may be increased locally by industrial contamination or drainage from arsenic-rich soils or rocks. Levels of arsenic in fresh waters vary widely, with high concentrations usually resulting from natural thermal activity, runoff and drainage from arsenic-contaminated watersheds. Typical concentrations of arsenic in fresh water range from 0.5 ppb to 2.4 ppb. Most of the arsenic carried into water is precipitated or absorbed on marine clays, phosphorites and hydrous oxides, resulting in sediment concentrations ranging from 7-29 ppm (freshwater sample) (Waldron, 1980).

##### Soil

Arsenic is ubiquitous in the earth's crust, occurring at general levels of 2-5 ppm. Exceptionally high concentrations occur in or over sulphide deposits where arsenic is present in relative abundance, averaging several hundred parts per million. Sedimentary rocks may have high concentrations of arsenic, especially if they contain manganese or iron oxides (Waldron, 1980). Arsenic entering the soil from the use of pesticides is on the decline because of the decreased use of sodium arsenate as a defoliant and replacement of lead arsenate with carbamates and organophosphates.

#### Biota

Arsenic is found in all living organisms. It is found in plants with concentrations ranging from 0.01 ppm to 5 ppm (dry weight), in earthworms at concentrations of 20 ppm, and in humans at 0.3 ppm (mostly in the hair and nails). Marine organisms have the highest concentrations of arsenic found in living organisms, with concentrations ranging from 0.5-50 ppm (lobsters). Bioaccumulation is most significant at lower trophic levels, with high toxicity lowering overall accumulation by marine organisms (Callahan, 1979). Arsenic is metabolized by a number of organisms to organic arsenicals, thereby increasing its mobility in the environment.

#### Other

Arsenic can be present in food as a contaminant or as a residue of lead or calcium arsenate used as insecticides, particularly on potatoes and fruit. Arsenic was found in 3.2% of food item samples examined in the U.S. during a market-basket survey, residues ranged from 0.1-4.7 mg/kg. Arsenic derived from insecticides has been detected in small quantities in tobacco smoke (IARC, 1973).

### INDUSTRIAL DATA

#### Production

Production in North Carolina was reported for one arsenic compound in the U.S. EPA Toxic Substances Control Act (TSCA) Chemical Substances Inventory:

Arsenic acid (07778-39-4) Mineral Research, Concord, N.C.

No report of production volume was given. (U.S. EPA, TSCA Inventory, 1980).

Arsenic production in the U.S. is small with only one major U.S. producer. Almost all of the arsenic used in this country is imported from Sweden. Imports for 1978 were estimated at 335,000 kg (740,000 lbs) (IARC, 1980).

Estimated U.S. Consumption in 1978:

Alloying additive	90 percent
Electronic devices	7 percent
Veterinary medicines	3 percent

(IARC, 1980)

Reported uses of arsenic and the corresponding SIC codes are listed below:

In alloys, especially for hardening copper and lead.  
In semiconductors and other electronic components.  
In veterinary medicines for producing arsenic compounds.  
In special types of glass.  
As a radioactive isotope, is used in toxicological research.  
(IARC, 1980, Merck, 1976)

Chemical synthesis, analytical reagent 28  
(Arsenic acid, pentoxide, trioxide, sodium arsenate, trichloride)

Pesticides, including herbicides, 2879  
insecticides, fungicides, rodenticides and cotton defoliants:  
(trioxide, pentoxide, calcium arsenate and arsenite, sodium arsenate and arsenite, potassium arsenate, dimethyl arsonic acid, methane arsonic acid and its sodium salt, zinc metaarsenite)

Pharmaceuticals  
(Arsenilic acid, arsonoacetic acid disodium salt, ethane arsonic acid, lead arsenate, potassium arsenate, sodium arsenite, diammonium arsenate, arsenic trioxide)

Semiconductors  
(trisulfide, arsine gas, gallium arsenide, indium arsenide)

Wood preservatives  
(pentoxide, sodium arsenate and arsenite)

Corrosion inhibitor  
(sodium arsenite)

Leather tanning  
(trisulfide, trioxide, potassium arsenate, sodium arsenite)

Textile dyes, mordants  
(trioxide, sodium arsenite, potassium arsenate)

Pigments  
(trisulfide, disulfide, pentasulfide, sodium arsenite)

Glass, lenses, ceramics, mirrors  
(trisulfide, trioxide, hemiselenide, pentoxide, trichloride potassium arsenite, cobaltous arsenate)

Pyrotechnics (trisulfide)

Adhesives (Pentoxide)

Metallurgy (trioxide)

Paper (potassium arsenate)  
(IARC, 1980, Merck, 1976)

### RESEARCH AND REGULATORY DATA

#### Existing Guidelines and Standards

##### Ambient Air

Under evaluation for possible designation as a Hazardous Air Pollutant by the U.S. Environmental Protection Agency.

##### Workroom Air

ACGIH The Threshold Limit Value (TLV) established by the American Conference of Governmental Industrial Hygienists (ACGIH) for workroom air is 200 µg/cu m as a time-weighted average.

NIOSH The National Institute of Occupational Safety and Health (NIOSH) recommends a standard of 2 µg/cu m as a time-weighted average.

OSHA The Occupational Safety and Health Administration's (OSHA) standard for workroom air is 500 µg/cu m as a time-weighted average.

#### Water

Addressed by National Interim Primary Drinking Water Regulations set by the U.S. Environmental Protection Agency.

Addressed by Ambient Water Quality Criteria set by the U.S. Environmental Protection Agency.

Designated a toxic pollutant by the U.S. Environmental Protection Agency.

#### Other

Regulated as a hazardous material by the U.S. Department of Transportation.

Regulated as a hazardous waste under the Hazardous Waste Management System by the U.S. Environmental Protection Agency.

Addressed by Rebuttable Presumption Against Registration (RPAR) through the U.S. Environmental Protection Agency.

#### Agencies Concerned with this Chemical

Subject of a monograph prepared by the International Agency for Research on Cancer (IARC).

Addressed by a development plan prepared by the Interagency Regulatory Liaison Group (IRLG).

Addressed by a National Toxicology Program (NTP) Executive Summary and included in the list of 100 compounds nominated for NTP testing.

#### REFERENCES

American Conference of Governmental Industrial Hygienists (ACGIH). Documentation of the Threshold Limit Values, Fourth Edition. Cincinnati, OH (1980).

Interagency Regulatory Liaison Group (IRLG). Excerpt on Arsenic. Regulator Reporter, Volume 11, Issue 1.

International Agency for Research on Cancer. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, Lyon, France, Volume 23. A World Health Organization Publication (WHO), Geneva (1981).

MEDLARS II Toxicology Data Bank (TDB) record of Arsenic. National Library of Medicine (May 1981).

Michigan Department of Natural Resources, Environmental Protection Bureau. Michigan Critical Materials Register 1980. Hazard Assessment Sheet for Arsenic. Lansing, Michigan (1980).

National Institute of Occupational Safety and Health (NIOSH). Criteria for a Recommended Standard...Occupational Exposure to Arsenic. U.S. Department of Health, Education, and Welfare. DHEW (NIOSH) Publication No. 76-129 (1975).

National Toxicology Program (NTP). Executive Summary for Arsenic. In Executive Summaries of Arsenic Compounds Nominated for FY 81 Testing. U.S. Department of Health, Education, and Welfare, Jefferson, Arkansas (1980).

Occupational Safety and Health Administration (OSHA). Candidate Substance Data Summary Sheet. Chemical: Arsenic Compounds.

U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances. Chemical Hazard Information Profiles (CHIPs). EPA-560/11-80-011 (1980).

U.S. Environmental Protection Agency, Carcinogen Assessment Group (CAG). Carcinogen Assessment Group's Preliminary Risk Assessment on Arsenic Compounds, Washington, DC (February 11, 1980).

U.S. Environmental Protection Agency, Office of Water Planning and Standards. Ambient Water Quality Criteria for Arsenic. EPA/440-4-80-016 (October 1980).

Venugopal, and Luckey, 1978 Metal Toxicology in Mammals-2, Plenum Press, New York.

Waldron, H.A. 1980 Metals in the Environment, Academic Press, New York.

# Occupational Health Guideline for Soluble Barium Compounds (as Barium)

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to all soluble barium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Barium nitrate

- Formula:  $\text{Ba}(\text{NO}_3)_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

### Barium oxide

- Formula:  $\text{BaO}$
- Synonyms: None
- Appearance and odor: Odorless white solid.

### Barium carbonate

- Formula:  $\text{BaCO}_3$
- Synonyms: None
- Appearance and odor: Odorless white solid.

### Barium chloride

- Formula:  $\text{BaCl}_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble barium compounds is 0.5 milligram of soluble barium compounds per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Soluble barium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

### • Effects of overexposure

1. *Short-term Exposure:* Soluble barium compounds may cause local irritation of the eyes, nose, throat, bronchial tubes, and skin. Soluble barium compounds may also cause severe stomach pains, slow pulse rate, irregular heart beat, ringing of the ears, dizziness, convulsions, and muscle spasms. Death may occur.

2. *Long-term Exposure:* None known

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble barium compounds.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to soluble barium compounds at potentially hazardous levels:

#### 1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the heart, lungs, and nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Soluble barium compounds cause human lung damage. Surveillance of the lungs is indicated.

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations

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Public Health Service    Centers for Disease Control  
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U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration



—FVC and FEV (1 sec): Soluble barium compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Electrocardiogram: Barium compounds may cause cardiac arrhythmias and may have a direct effect on the cardiac muscle. Periodic surveillance of the heart is indicated.

**2. Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

• **Summary of toxicology**

Soluble barium salts cause severe gastroenteritis and systemic effects by ingestion. Intravenous injection of barium compounds in animals causes a strong, prolonged stimulation of muscle resulting in hyperperistalsis, bladder contraction, vasoconstriction, and irregular contraction of the heart followed by arrest in systole. Animals also exhibit stimulation of the central nervous system followed by paralysis. Ingestion of barium carbonate by humans causes gastroenteritis, muscular paralysis, slow pulse rate, extrasystoles, and hypokalemia. Heavy industrial exposure to dusts of barium sulfate or barium oxides may produce a benign pneumoconiosis, termed baritosis. It results in no impairment of ventilatory function, although signs of mild bronchial irritation may occur. Characteristic x-ray changes are those of small, dense, circumscribed nodules evenly distributed throughout the lung fields, reflecting the radio-opacity of the barium dust. Bronchial irritation has been reported from the inhalation of barium carbonate dust. Barium hydroxide and barium oxide are strongly alkaline in aqueous solution, causing severe burns of the eye and irritation of the skin.

## CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Barium nitrate**

1. Molecular weight: 261.4
2. Boiling point (760 mm Hg): Greater than 592 C (greater than 1098 F) (decomposes)
3. Specific gravity (water = 1): 3.24
4. Vapor density (air = 1 at boiling point of barium nitrate): Not applicable
5. Melting point: 592 C (1098 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 9.2
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium oxide**

1. Molecular weight: 153.3
2. Boiling point (760 mm Hg): 2000 C (3632 F)
3. Specific gravity (water = 1): 5.72
4. Vapor density (air = 1 at boiling point of barium oxide): Not applicable
5. Melting point: 1921 C (3490 F)

6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F):

Reacts

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium carbonate**

1. Molecular weight: 197.3
2. Boiling point (760 mm Hg): 1300 C (2372 F) (decomposes)
3. Specific gravity (water = 1): 4.25
4. Vapor density (air = 1 at boiling point of barium carbonate): Not applicable
5. Melting point: Decomposes at 1300 C (2372 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0022

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium chloride**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 1560 C (2840 F)
3. Specific gravity (water = 1): 3.86
4. Vapor density (air = 1 at boiling point of barium chloride): Not applicable
5. Melting point: 963 C (1765 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 36

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: For barium nitrate, elevated temperatures may cause melting and decomposition; for the other compounds, none hazardous.

2. Incompatibilities: Contact of barium oxide with water, carbon dioxide, or hydrogen sulfide may cause fires and explosions. Contact of barium carbonate with acids causes formation of carbon dioxide gas that may cause suffocation in enclosed spaces. Contact of barium nitrate with organic matter and combustible materials may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving barium nitrate.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For barium nitrate, data not available; for the other compounds, not applicable.
3. Flammable limits in air, % by volume: Not applicable

4. Extinguishant: Large amounts of water should be used on adjacent fires

• **Warning properties**

According to Grant, barium chloride causes "considerable iritis, which subsides in a few days" when "tested

in neutral 0.08 to 0.1 M solution on rabbit eyes by injection into the cornea or by dropping for 10 minutes on the eye after the corneal epithelium was removed to facilitate penetration." Grant states that "both the oxide and hydroxide are capable of causing severe alkali burns of the eye, similar to those produced by calcium hydroxide."

## MONITORING AND MEASUREMENT PROCEDURES

### • General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Method

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by leaching in hot water, solution of sample in acid, and analysis in an atomic absorption spectrophotometer. An analytical method for soluble barium compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent repeated or prolonged skin contact with barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds.

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with barium oxide or liquids containing barium oxide, where skin contact may occur.

- If employees' clothing has had any possibility of being contaminated with barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.

- Where exposure of an employee's body to barium oxide or liquids containing barium oxide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be removed promptly and not reworn until the contaminant is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of barium oxide or liquids containing barium oxide contacting the eyes.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to barium oxide or liquids containing barium oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Workers subject to skin contact with barium oxide or liquids containing barium oxide should wash any areas of the body which may have contacted barium oxide at the end of each work day.

- Skin that becomes contaminated with barium carbonate, barium chloride, or barium nitrate should be promptly washed or showered to remove any contaminant. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

- Skin that becomes contaminated with barium oxide should be promptly washed or showered to remove any barium oxide from the skin after all obvious amounts of barium oxide have been removed by other means (e.g., by use of oil or vaseline). Employees who are being burned by barium oxide should immediately utilize quick drenching facilities without first removing barium oxide by other means.
- Eating and smoking should not be permitted in areas where solid barium carbonate, barium chloride, barium nitrate, or barium oxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble barium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and distribution of soluble barium compounds	Process enclosure; local exhaust ventilation
Use in manufacture of pressed and blown glassware and flint and crown optical glass; manufacture of ceramic products; use in electronics industry in manufacture of magnets, vacuum tubes, cathodes, x-ray fluorescent screens, TV picture tubes, and dry cell depolarizers	Process enclosure; local exhaust ventilation
Use in manufacture of photographic papers, dyes, and chemicals	Process enclosure; local exhaust ventilation
Use as pesticides, rodenticides, and disinfectants; use in manufacture of explosives, matches, and pyrotechnics as igniter compositions and fireworks	Process enclosure; local exhaust ventilation

## Operation

## Controls

Use as an additive in manufacture of grease, and manufacture of lubricating oils; use in refining of vegetable and animal oils

Process enclosure;  
local exhaust ventilation

Use in case-hardening of steel in metallurgy; in welding aluminum; in electroplating; and in aluminum and sodium refining

Process enclosure;  
local exhaust ventilation

Use in water treatment and boiler compounds for softening water; use as catalysts, analytical reagents, and purifying agents

Process enclosure;  
local exhaust ventilation

Use for treatment of textiles, leather, and rubber; use in manufacture of paper and cellulose as a bleaching agent; use in manufacture of pigments, colors, and lakes

Process enclosure;  
local exhaust ventilation

Use as a depilatory in processing of hides; as a fire-proof and extinguishing agent; in embalming; in sugar refining; in gas and solvent drying; in marble substitutes; in valve manufacture; and as a smoke suppressant in diesel fuels

Process enclosure;  
local exhaust ventilation

Use in manufacture of pigments, paints, enamels, and printing inks

Process enclosure;  
local exhaust ventilation

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If solutions of barium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

#### • Skin Exposure

If solutions of barium compounds get on the skin, immediately flush the contaminated skin with water. If solutions of barium compounds soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

#### • Breathing

If a person breathes in large amounts of soluble barium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

#### • Swallowing

When soluble barium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

#### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

### SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If soluble barium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble barium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Soluble barium compounds may be disposed of in sealed containers in a secured sanitary landfill.

### REFERENCES

- American Conference of Governmental Industrial Hygienists: "Barium and Compounds (as Ba)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Barium and Its Inorganic Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1962.
- Baskin, A. D. (ed.): *Handling Guide for Potentially Hazardous Commodities*, Railway Systems and Management Association, Chicago, 1972.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Jacobs, M.: *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, Interscience, New York, 1956.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.
- Thienes, C. H., and Haley, T. J.: *Clinical Toxicology* (5th ed.), Lea and Febiger, Philadelphia, 1972.

## RESPIRATORY PROTECTION FOR SOLUBLE BARIUM COMPOUNDS (AS BARIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m <sup>3</sup>
Particulate Concentration	
2.5 mg/m <sup>3</sup> or less	Any dust and mist respirator, except single-use.**
5 mg/m <sup>3</sup> or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m <sup>3</sup> or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 250 mg/m <sup>3</sup> or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

\*\*If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

# Occupational Health Guideline for Cadmium Dust (as Cadmium)\*

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to all cadmium dust. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Cadmium metal dust

- Formula: Cd
- Synonyms: None
- Appearance and odor: Odorless, gray powder.

### Cadmium oxide dust

- Formula: CdO
- Synonyms: None
- Appearance and odor: Odorless, brown solid or blue-black solid.

### Cadmium sulfide dust

- Formula: CdS
- Synonyms: Greenockite
- Appearance: Yellow-orange solid.

### Cadmium chloride dust

- Formula: CdCl<sub>2</sub>
- Synonyms: None
- Appearance: White solid

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium dust is 0.2 milligram of cadmium dust per cubic meter of air (mg/m<sup>3</sup>) averaged over an eight-hour work shift, with a ceiling level of 0.6 mg/m<sup>3</sup>. NIOSH has recommended that the permissible exposure limit be reduced to 40 micrograms of cadmium per cubic meter of air (μg/m<sup>3</sup>) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 200 μg/m<sup>3</sup> averaged over a 15-minute period. The recommendations in this guideline supplement the recommendations in the NIOSH Criteria Document for Cadmium, which should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Cadmium dust can affect the body if it is inhaled. It can also affect the body if it is swallowed.

### • Effects of overexposure

1. *Short-term Exposure:* Cadmium dust may cause irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur. Ingestion of cadmium dust may cause nausea, vomiting, diarrhea, and abdominal cramps.

2. *Long-term Exposure:* Repeated or prolonged exposure to cadmium dust may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium has also been reported to cause an increased incidence of cancer of the prostate in man. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium dust.

### • Recommended medical surveillance

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

The following medical procedures should be made available to each employee who is exposed to cadmium dust at potentially hazardous levels:

**1. Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, liver, kidneys, prostate, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. In addition, the urine should be examined for low molecular weight proteins by use of 3% sulfosalicylic or other acceptable techniques.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

**2. Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease. Urine protein measurements should be made available every four months.

• **Summary of toxicology**

Cadmium dust causes both acute and chronic effects. It is less toxic than cadmium fume, because dust has a larger particle size than fume; at high concentrations of the dust, physiologic effects similar to those arising from fume exposure could be expected. The acute effects primarily involve the lungs but may also affect other organ systems. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m<sup>3</sup> for 1 hour, or 9 mg/m<sup>3</sup> for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m<sup>3</sup>, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristic nasopharyngeal irritation followed by a feeling of chest constriction or substernal pain, with persistent cough and dyspnea; there may also be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop and progress rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. Cyanosis may be intense. In about 20% of the cases the dyspnea is progressive,

accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days after exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Absorbed cadmium is retained to a large extent by the body, and excretion is very slow. Continued exposure to low levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of an emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of water, beans, and rice contaminated with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; severe pain in the back and joints, a waddly gait, osteomalacia, spontaneous fractures, and occasional fatal renal failure are characteristics of the disorder, which has been termed "itai-itai." Subcutaneous injection of cadmium metal suspended in fowl serum produced rhabdomyosarcomata in rats; cadmium sulfate in sterile distilled water produced sarcomata; and cadmium chloride solution produced pleomorphic sarcomata at the injection site. Increased incidence of prostatic cancer has been reported following occupational exposure to cadmium. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring; acute necrosis of rat testes follows large doses orally or parenterally, but testicular effects have not been reported in humans.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data—Cadmium metal dust

1. Molecular weight: 112.4
2. Boiling point (760 mm Hg): 767 C (1412 F)
3. Specific gravity (water = 1): 8.642
4. Vapor density (air = 1 at boiling point of cadmium metal dust): Not applicable
5. Melting point: 321 C (609 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Cadmium oxide dust

1. Molecular weight: 128.4
2. Boiling point (760 mm Hg): 900 C (1652 F) (sublimes and decomposes)
3. Specific gravity (water = 1): 6.95 or 8.15
4. Vapor density (air = 1 at boiling point of cadmium oxide dust): Not applicable
5. Melting point: 900 C (1652 F) (sublimes and decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0005
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Cadmium sulfide dust

1. Molecular weight: 144.5
2. Boiling point (760 mm Hg): Sublimes in N<sub>2</sub> at 980 C (1796 F)
3. Specific gravity (water = 1): 4.82
4. Vapor density (air = 1 at boiling point of cadmium sulfide dust): Not applicable
5. Melting point: 1750 C (3182 F) at 100 atm.
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0001
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Cadmium chloride dust

1. Molecular weight: 183
2. Boiling point (760 mm Hg): 960 C (1760 F)
3. Specific gravity (water = 1): 4.047
4. Vapor density (air = 1 at boiling point of cadmium chloride dust): Not applicable
5. Melting point: 568 C (1054 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 140
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of cadmium metal dust with strong oxidizers or with elemental sulfur, selenium, and tellurium may cause fires and explosions

3. Hazardous decomposition products: Toxic gases and vapors (such as cadmium oxide fume) may be released in a fire involving cadmium dust.

4. Special precautions: None

### • Flammability

1. Flash point: Not applicable
2. Autoignition temperature: 250 C (482 F) (layer) (cadmium metal dust)
3. Minimum explosive dust concentration: Data not available
4. Extinguishant: Dry powder for metal fires

### • Warning properties

Grant states that "cadmium is a very toxic metal which gives off fumes when burned or heated strongly. Characteristically these fumes cause dryness and irritation of the throat, followed in a few hours by nausea and diarrhea. Smarting of the eyes occurs relatively infrequently, and no injury to the eyes of human beings has been reported. Neither eye nor respiratory irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

## MONITORING AND MEASUREMENT PROCEDURES

### • Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cadmium dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

### • Method

Sampling and analyses may be performed by collection of cadmium dust on a filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for cadmium dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).



## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- If employees' clothing has had any possibility of being contaminated with cadmium dust, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with cadmium dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cadmium dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cadmium dust, the person performing the operation should be informed of cadmium dust's hazardous properties.
- Employees should be provided with and required to use dust-resistant safety goggles where there is any possibility of cadmium chloride dust contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to cadmium chloride dust, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Workers subject to skin contact with cadmium dust should wash with soap or mild detergent and water any areas of the body which may have contacted cadmium dust at the end of each work day.
- Eating and smoking should not be permitted in areas where cadmium dust is handled, processed, or stored.
- Employees who handle cadmium dust should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fabrication of cadmium-plated marine, aircraft, and motor vehicle equipment for corrosion-resistant coatings	Local exhaust ventilation; personal protective equipment
Liberation during processing of cadmium metal	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation in synthesis of cadmium compounds	Process enclosure; local exhaust ventilation
Liberation in manufacture and fabrication of cadmium alloys; recovery from flue dusts during smelting of lead and zinc operations	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of nuclear reactor rods	Process enclosure; local exhaust ventilation

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If cadmium dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

### • Skin Exposure

If cadmium dust gets on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the close of work.

### • Breathing

If a person breathes in large amounts of cadmium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

When cadmium dust or liquids containing cadmium dust have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the

person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.

- If cadmium dust is released in hazardous concentrations, the following steps should be taken:

1. Remove all ignition sources.

2. Ventilate area of release.

3. Collect released material in the most convenient and safe manner for reclamation or for disposal in sealed containers in a secured sanitary landfill.

- Waste disposal method:

Cadmium dust may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Cadmium Dust," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Cadmium," *Hygienic Guide Series*, Detroit, Michigan, 1962.
- American National Standard Acceptable Concentrations - Cadmium Dust: ANSI-Z37.5-1970, American National Standards Institute, Inc., New York, 1970.
- Bonnell, J. A.: "Cadmium Poisoning," *Annals of Occupational Hygiene*, 8:45-49, 1965.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Dunphy, B.: "Acute Occupational Cadmium Poisoning: A Critical Review of the Literature," *Journal of Occupational Medicine*, 9:22-26, 1967.
- Emmerson, B. T.: "'Ouch-Ouch' Disease: The Osteomalacia of Cadmium Nephropathy," *Annals of Internal Medicine*, 73:854-855, 1970.
- Fassett, D. W.: "Cadmium: Biological Effects and Occurrence in the Environment," *Annual Review of Pharmacology*, 15:425-435, 1975.

- Friberg, L., et al.: *Cadmium in the Environment*, (2nd ed.), CRC Press, Cleveland, 1974.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

- Gunn, S. A., et al.: "Specific Response of Mesenchymal Tissue to Cancerigenesis by Cadmium," *Archives of Pathology*, 83:493-499, 1967.

- Haddow, A., et al.: "Cadmium Neoplasia: Sarcomata at the Site of Injection of Cadmium Sulphate in Rats and Mice," *British Journal of Cancer*, 18:667-673, 1964.

- Heath, J. C., et al.: "Cadmium as a Carcinogen," *Nature*, 193:592-593, 1962.

- Holmberg, R. E., Jr., and Ferm, V. H.: "Interrelationships of Selenium, Cadmium, and Arsenic in Mamalian Teratogenesis," *Archives of Environmental Health*, 18:873-877, 1969.

- Karolinska Institute: *Cadmium in the Environment, II*, PB-221 198, prepared for Environmental Protection Agency, National Technical Information Service, Springfield, Virginia, 1973.

- Louria, D. B., et al.: "The Human Toxicity of Certain Trace Elements," *Annals of Internal Medicine*, 76:307-319, 1972.

- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . . Occupational Exposure to Cadmium*, HEW Publication No. (NIOSH) 76-192, GPO No. 017-033-00206-1, U.S. Government Printing Office, Washington, D.C., 1976.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

- Stauden, A. (ex. ed.): *Kirk-Othmer Encyclopedia of Chemical Technology*, (2nd ed.), Interscience, New York, 1972.

- Tsuchiya, K.: "Proteinuria of Workers Exposed to Cadmium Fume," *Archives of Environmental Health*, 14:875-880, 1967.

## \* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

## RESPIRATORY PROTECTION FOR CADMIUM DUST (AS CADMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m <sup>3</sup>
Dust Concentration	
1 mg/m <sup>3</sup> or less	Any dust respirator, except single-use.
2 mg/m <sup>3</sup> or less	Any dust respirator, except single-use or quarter-mask respirator. Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m <sup>3</sup> or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m <sup>3</sup> or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

# Occupational Health Guideline for Cadmium Fume

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula: Cd/CdO
- Synonyms: None
- Appearance: Finely divided solid particles dispersed in air.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium fume is 0.1 milligram of cadmium fume per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift, with an acceptable ceiling level of  $0.3 \text{ mg}/\text{m}^3$ . NIOSH has recommended that the permissible exposure limit be reduced to a time-weighted average of 40 micrograms cadmium per cubic meter ( $\text{ug}/\text{m}^3$ ) with a ceiling level of  $200 \text{ ug cadmium}/\text{m}^3$  for a 15-minute period. The NIOSH Criteria Document for Cadmium should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Cadmium fume can affect the body if it is inhaled.

### • Effects of overexposure

1. *Short-term Exposure:* Cadmium fume causes irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur.

2. *Long-term Exposure:* Repeated or prolonged exposure to cadmium fume may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphyse-

ma), kidney damage, and mild anemia. Exposure to cadmium fume has also been reported to cause an increased incidence of cancer of the prostate in men. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring. This effect has not been reported in humans.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium fume.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to cadmium fume at potentially hazardous levels:

#### 1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, kidneys, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be examined for the specific protein.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service    Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

Urine protein measurements should be made available every four months.

#### • Summary of toxicology

Cadmium fume (cadmium oxide) is a severe pulmonary irritant that has caused fatal pulmonary edema in workers; chronic exposures may lead to severe pulmonary emphysema. Cadmium sulfide produces malignant tumors in animals by injection, suggesting that cadmium is carcinogenic. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m<sup>3</sup> for 1 hour, or 9 mg/m<sup>3</sup> for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m<sup>3</sup>, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristically nasopharyngeal irritation, followed by a feeling of chest constriction or substernal pain, with cough and dyspnea; there also may be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days of exposure: at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Continued exposure to lower levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with evidence of renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. Cadmium absorbed by any route is, to a very large extent, retained by the body. Excretion is very slow. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of beans, rice and water contaminated

with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; pain in the back and joints, an unsteady gait, osteomalacia, bone fractures, and occasional renal failure are characteristics of the disorder. Rats, injected subcutaneously with cadmium metal suspended in fowl serum, produced rhabdomyosarcomata; with cadmium sulfate in sterile distilled water, sarcomata; and with cadmium chloride solution, pleomorphic sarcomas at the injection site, suggesting that cadmium is carcinogenic. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring. Increased prostatic and lung cancer has been reported in humans exposed to cadmium oxide. Acute necrosis of the rat testis follows large doses orally or parenterally.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 112—128
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of cadmium fume): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity

1. Not applicable

### • Flammability

1. Not applicable

### • Warning properties

Grant reports that "smarting of the eyes occurs relatively infrequently (upon exposure to cadmium fume), and no injury to the eyes of human beings has been reported. Neither eye nor respiratory tract irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

## MONITORING AND MEASUREMENT PROCEDURES

### • Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of cadmium fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of cadmium fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for cadmium fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## SANITATION

- Eating and smoking should not be permitted in areas where fumes may be generated in the handling or processing of cadmium

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium fume may occur and control methods which may be effective in each case:

### Operation

Liberation during smelting and refining of ores where it is a by-product of zinc, lead, and copper-bearing ores

Liberation during recovery of metal by processing of scrap; during melting and pouring of cadmium metal; during casting of alloys for cadmium-copper, cadmium-lead, cadmium-bismuth, cadmium-silver, cadmium-nickel, cadmium-lead-silver, cadmium-lead-silver-nickel, cadmium-lead-bismuth-tin, and cadmium-gold products used for coating telephone cables, trolley wires, welding electrodes, automatic sprinkling systems, steam boilers, fire alarms, high-pressure/temperature bearings, starting switches, aircraft relays, light-duty circuit breakers, low-temperature solder, and jewelry

Liberation during fabrication of metal, alloys, or plated steel

Liberation during casting and use of solders; during melting of cadmium ingots for paint and pigment manufacture used for coloring of plastics and ceramic glazes, electroplating, and in chemical synthesis

Liberation during coating on metals by hot dipping or spraying

### Controls

Process enclosure; local exhaust ventilation; personal protective equipment

Process enclosure; local exhaust ventilation; personal protective equipment

Process enclosure; local exhaust ventilation; personal protective equipment

Process enclosure; local exhaust ventilation; personal protective equipment

Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during manufacture of nickel-cadmium batteries for use in radio-portable telephones, convenience appliances, and vented cells used in air planes, helicopters, and stand-by power and lighting

Process enclosure; local exhaust ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Breathing

If a person breathes in large amounts of cadmium fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of cadmium fume are inadvertently released, ventilate the area of the release to disperse the fume.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Cadmium and Compounds as Cd," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Cadmium," *Hygienic Guide Series*, Detroit, Michigan, 1963.
- Bonnell, J. A.: "Cadmium Poisoning," *Annals of Occupational Hygiene*, 8:45-50, 1965.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Dunphy, B.: "Acute Occupational Cadmium Poisoning: A Critical Review of the Literature," *Journal of Occupational Medicine*, 9:22-26, 1967.
- Emmerson, B. T.: "'Ouch-Ouch' Disease: The Osteomalacia of Cadmium Nephropathy," *Annals of Internal Medicine*, 73:854-855, 1970.
- Fassett, D. W.: "Cadmium: Biological Effects and Occurrence in the Environment," *Annual Review of Pharmacology*, 15:425-435, 1975.
- Fleischer, M., et al.: "Environmental Impact of Cadmium: A Review by the Panel on Hazardous Trace Substances," *Environmental Health Perspectives*, 253-323, May 1974.
- Friberg, L., et al.: *Cadmium in the Environment*, (2nd ed.), CRC Press, Cleveland, 1974.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Gunn, S. A., et al.: "Specific Response of Mesenchymal Tissue to Cancerogenesis by Cadmium," *Archives of Pathology*, 83:493-499, 1967.
- Haddow, A., et al.: "Cadmium Neoplasia: Sarcomata at the Site of Injection of Cadmium Sulphate in Rats and Mice," *British Journal of Cancer*, 18:667-673, 1964.
- Heath, J. C., et al.: "Cadmium as a Carcinogen," *Nature*, 193:592-593, 1962.
- Holmberg, E. R., Jr., and Ferm, V. H.: "Interrelationships of Selenium, Cadmium, and Arsenic in Mammalian Teratogenesis," *Archives of Environmental Health*, 18:873-877, 1969.
- Louria, D. B., et al.: "The Human Toxicity of Certain Trace Elements," *Annals of Internal Medicine*, 76:307-319, 1972.
- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . Occupational Exposure to Cadmium*, HEW Publication No. (NIOSH) 76-192, GPO No. 017-033-00206-1, U.S. Government Printing Office, Washington, D.C., 1976.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Tsuchiya, K.: "Proteinuria of Workers Exposed to Cadmium Fume," *Archives of Environmental Health*, 14:875-880, 1967.

## \* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*. Volume 2, 1973, and Volume 11, 1976.

## RESPIRATORY PROTECTION FOR CADMIUM FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m <sup>3</sup>
Particulate Concentration	
1 mg/m <sup>3</sup> or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m <sup>3</sup> or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m <sup>3</sup> or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

\*Only NIOSH-approved or MSHA-approved equipment should be used.



# Occupational Health Guideline for Chromium Metal and Insoluble Chromium Salts\*

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to all chromium metal and insoluble chromium salts. Physical and chemical properties of some specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Metallic chromium

- Formula: Cr
- Synonyms: None
- Appearance and odor: Shiny, odorless metal.

### Copper chromite

- Formula:  $\text{Cu}_2\text{Cr}_2\text{O}_4$
- Synonyms: Cuprous chromite
- Appearance and odor: Greenish-blue, odorless solid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromium metal or insoluble chromium salts is 1 milligram of chromium metal or insoluble chromium salts per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium,

cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to  $0.001 \text{ Cr (VI) mg}/\text{m}^3$  and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to  $0.025 \text{ Cr (VI) mg}/\text{m}^3$  averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of  $0.05 \text{ Cr (VI) mg}/\text{m}^3$  averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

- **Routes of exposure**  
Chromium metal or insoluble chromium salts can affect the body if they are inhaled. They can also affect the body if they are swallowed.
- **Effects of overexposure**  
Ferro chrome alloys have been associated with lung changes in workers exposed to these alloys. Chromite dust exposure may cause minor lung changes.
- **Reporting signs and symptoms**  
A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chromium metal or insoluble chromium salts.
- **Recommended medical surveillance**  
The following medical procedures should be made available to each employee who is exposed to chromium metal or insoluble chromium salts at potentially hazardous levels:

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service    Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

### 1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Chromium and its insoluble salts may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Insoluble chromium salts are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

### • Summary of toxicology

The dusts of chromium metal and its insoluble salts, chiefly the chromites, are usually reported to be relatively nontoxic; this is debatable, since exposures associated with toxic effects are usually mixed exposures involving several hexavalent chromium compounds. Ferrochrome alloys have been associated with pulmonary disease in humans. Four workers engaged in the production of ferrochrome alloys developed a nodular type of pulmonary disease with impairment of pulmonary function; air concentrations of chromium in this study averaged 0.26 mg/m<sup>3</sup>, although other fumes and dusts were also present. This pulmonary problem may be one of hypersensitivity and thus reversible. Other reports state that chest roentgenograms have revealed only "exaggerated pulmonic markings" in workers exposed to chromite dust. The lungs of groups of workers exposed to chromite dust have been shown to be the seat of pneumoconiotic changes consisting of slight thickening of interstitial tissue and interalveolar septa, with histologic fibrosis and hyalinization. Chromite ore roast mixed with sheep fat implanted intrapleurally in rats produced squamous cell carcinomata coexisting with sarcomata of the lungs; the same material implanted in the thighs of rats produced fibrosarcomata. A refractory plant using chromite ore to make chromite brick had no excess of lung cancer deaths over a 14-year period, and it was concluded that chromite alone probably is not carcinogenic.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data—Metallic chromium

1. Molecular weight: 52
2. Boiling point (760 mm Hg): 2640 C (4784 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of metallic chromium): Not applicable
5. Melting point: 1900 C (3452 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Copper chromite

1. Molecular weight: 295.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 5.24
4. Vapor density (air = 1 at boiling point of copper chromite): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Basic potassium zinc chromate

1. Molecular weight: 873.8
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 3.47
4. Vapor density (air = 1 at boiling point of basic potassium zinc chromate): Not applicable
5. Melting point: Loses water slowly above 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Chromium metal in contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None listed.
4. Special precautions: None listed.

### • Flammability

1. Flash point: Not applicable
2. Minimum ignition temperature (metal): 400 C (752 F) (layer); 580 C (1076 F) (cloud)
3. Minimum explosive dust concentration (metal): 230 grams/m<sup>3</sup>
4. Extinguishant: Dry sand, dry dolomite, dry graphite

### • Warning properties

Chromium metal and insoluble salts are not known to be eye irritants.

## MONITORING AND MEASUREMENT PROCEDURES

### • Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of chromium metal or insoluble chromium salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

#### • Method

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for chromium metal and insoluble chromium salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing insoluble chromium salts.

- Clothing contaminated with insoluble chromium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of insoluble chromium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the insoluble chromium salts, the person

performing the operation should be informed of insoluble chromium salts's hazardous properties.

- Non-impervious clothing which becomes contaminated with insoluble chromium salts should be removed promptly and not reworn until the insoluble chromium salts are removed from the clothing.

- Employees should be provided with and required to use dust- and splashproof safety goggles where solids or liquids containing insoluble chromium salts may contact the eyes.

## SANITATION

- Skin that becomes contaminated with insoluble chromium salts should be promptly washed or showered with soap or mild detergent and water to remove any insoluble chromium salts.

- Eating and smoking should not be permitted in areas where solids or liquids containing insoluble chromium salts are handled, processed, or stored.

- Employees who handle solids or liquids containing insoluble chromium salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromium metal or insoluble chromium salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in fabrication of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in preparation of alloy steels to enhance corrosion- and heat-resistance	Local exhaust ventilation; general dilution ventilation
Use in fabrication of plated products for decoration or increased wear-resistance	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of non-ferrous alloys to impart special qualities to the alloys	Local exhaust ventilation; general dilution ventilation
Use in production and processing of insoluble salts	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls
Use as chemical intermediates; use in textile industry in dyeing, silk treating, printing, and mothproofing wool	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in leather industry in tanning; use in photographic fixing baths	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons	Local exhaust ventilation; general dilution ventilation
Use as fuel additives and propellant additives; in photographic fixing baths and in ceramics	Local exhaust ventilation; general dilution ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If chromium metal or solids or liquids containing insoluble chromium salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

### • Skin Exposure

If solids or liquids containing insoluble chromium salts get on the skin, wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing insoluble chromium salts penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of chromium metal or insoluble chromium salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

When solids or liquids containing insoluble chromium salts have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If chromium metal or insoluble chromium salts are spilled, the following steps should be taken:

1. Remove all ignition sources where metallic chromium has been spilled.
2. Ventilate area of spill.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromium metal or insoluble chromium salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chromium metal or insoluble chromium salts may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chromium (as Cr)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Committee on Medical and Biologic Effects of Environmental Pollutants, Division of Medical Sciences, National Research Council: *Chromium*, National Academy of Sciences, Washington, D.C., 1974.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Hueper, W. C.: "Experimental Studies in Metal Carcinogenesis. X. Cancerigenic Effects of Chromite Ore Roast Deposited in Muscle Tissue and Pleural Cavity of Rats," *A.M.A. Archives of Industrial Health*, 18:284-291, 1958.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Johnstone, R. T., and Miller, S. E.: *Occupational Disease and Industrial Medicine*, Saunders, Philadelphia, 1960.
- Mancuso, T. F., and Hueper, W. C.: "Occupational Cancer and Other Health Hazards in a Chromate Plant: A Medical Appraisal - I. Lung Cancer in Chromate

Workers," *Industrial Medicine and Surgery*, 20:358-363, 1951.

- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . . Occupational Exposure to Chromic Acid*, HEW Publication No. HSM 73-11021, GPO No. 017-033-00020, U.S. Government Printing Office, Washington, D.C., 1973.

- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . . Occupational Exposure to Chromium (VI)*, HEW Publication No. (NIOSH) 76-129, GPO No. 017-033-00125-1, U.S. Government Printing Office, Washington, D.C., 1975.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

- Princi, F., et al.: "Pulmonary Disease of Ferroalloy Workers," *Journal of Occupational Medicine*, 4:301-310, 1962.

- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

- Thienes, C. H., and Haley, T. J.: *Clinical Toxicology* (5th ed.), Lea and Febiger, Philadelphia, 1972.

## \* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

### • Method

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic

## RESPIRATORY PROTECTION FOR CHROMIUM METAL AND INSOLUBLE CHROMIUM SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m <sup>3</sup>
Particulate Concentration	
5 mg/m <sup>3</sup> or less	Any dust and mist respirator.
10 mg/m <sup>3</sup> or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m <sup>3</sup> or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m <sup>3</sup> or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

# Occupational Health Guideline for Soluble Chromic and Chromous Salts (as Chromium)\*

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to all soluble chromic and chromous salts. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Chromic sulfate hydrate

- Formula:  $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  (approximately)
- Synonyms: None
- Appearance and odor: Violet or green, odorless solid.

### Chromic potassium sulfate

- Formula:  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
- Synonyms: Potassium chrome alum; potassium chromium (III) sulfate
- Appearance and odor: Red-violet, odorless solid.

### Chromous chloride

- Formula:  $\text{CrCl}_2$
- Synonyms: None
- Appearance and odor: Colorless to gray, odorless solid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble chromic or chromous salts is 0.5 milligrams of soluble chromic or

chromous salts (as chromium) per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: They are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to  $0.001 \text{ mg}/\text{m}^3$  and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to  $0.025 \text{ Cr (VI) mg}/\text{m}^3$  averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of  $0.05 \text{ Cr (VI) mg}/\text{m}^3$  averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Soluble chromic or chromous salts can affect the body if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

### • Effects of overexposure

Exposure to certain soluble chromic or chromous salts have been reported to cause an allergic skin rash.

### • Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble chromic or chromous salts.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service    Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble chromic and chromous salts at potentially hazardous levels:

1. **Initial Medical Screening:** Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble chromic and chromous salts exposure.

—Skin disease: Chromic salts may cause an allergic dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. **Periodic Medical Examination:** Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The soluble chromic and chromous salts have no established toxicity. Since exposures are often mixed, consideration should be given to the possible exposure to hexavalent chromium, which is a more toxic form. The compound hexaaquachromium trichloride has been found to react with protein in vitro, indicating that it is not biologically inert. Of 35 rats implanted with chromic acetate in the thigh muscle, 1 developed sarcoma; this was considered to be evidence of weak carcinogenicity of this soluble trivalent compound. When taken by mouth, the trivalent compounds do not give rise to local or systemic effects and are poorly absorbed; no specific effects are known to result from inhalation. Animals ingesting chromic salts showed one-ninth as much chromium in the tissues as did animals ingesting equal amounts of chromates. Dermatitis from some chromic salts has been reported. Some investigators believe that all persons sensitized to hexavalent chromium are also sensitive to the trivalent form, although this has not been firmly established.

## CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Chromic sulfate hydrate**

1. Molecular weight: 680 (approximately)
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of chromic sulfate hydrate): Not applicable
5. Melting point: 90 C (194 F) Loses water, residue does not melt
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 84–120
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Chromic potassium sulfate**

1. Molecular weight: 499.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.83

4. Vapor density (air = 1 at boiling point of chromic potassium sulfate): Not applicable

5. Melting point: 89 C (192 F) Loses water, then melts at 400 C (752 F)

6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)

7. Solubility in water, g/100 g water at 20 C (68 F): 19.6

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Chromous chloride**

1. Molecular weight: 122.9
2. Boiling point (760 mm Hg): 1300 C (2372 F)
3. Specific gravity (water = 1): 2.93
4. Vapor density (air = 1 at boiling point of chromous chloride): Not applicable
5. Melting point: 820 C (1508 F)
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Water (chromyl chloride)
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Most soluble chromic or chromous salts are not combustible. However, chromyl chloride reacts vigorously with water, forming chromic acid, chromic chloride, hydrochloric acid, and chlorine. Also, chromyl chloride causes ignition of ammonia, ethyl alcohol, turpentine, and other combustible materials.

- **Warning properties**

Grant states that "chromium compounds . . . are known to cause dermatitis, ulcers of the skin and mucous membranes, and perforation of the nasal septum." Chromium chloride is an example of the chromium compounds which Grant states produces these effects. Not all chromic and chromous salts produce eye irritation.

## MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of soluble chromic or chro-



mous salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

#### • Method

Sampling and analyses may be performed by collection of soluble chromic or chromous salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for soluble chromic and chromous salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

## RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquids or solids containing soluble chromic or chromous salts.

• Clothing contaminated with soluble chromic or chromous salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chromic or chromous salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic or chromous salts, the person performing the operation should be informed of soluble chromic or chromous salts's hazardous properties.

• Non-impervious clothing which becomes contaminated with soluble chromic or chromous salts should be removed promptly and not reworn until the soluble chromic or chromous salts are removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of liquids or solids containing soluble chromic or chromous salts contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquids or solids containing soluble chromic or chromous salts, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

• Skin that becomes contaminated with soluble chromic or chromous salts should be promptly washed or showered to remove any soluble chromic or chromous salts.

• Employees who handle liquids or solids containing soluble chromic or chromous salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble chromic or chromous salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile treatment in dyeing, printing, moth-proofing, and water-proofing; use in tanning of leather in gloves, garments, and shoe uppers	Local exhaust ventilation; personal protective equipment
Use in manufacture of pigments for green varnishes, inks, paints, and glazes	Local exhaust ventilation; personal protective equipment
Use for metal treatment and polishing	Local exhaust ventilation; personal protective equipment
Use in photographic fixing baths for hardening of emulsions; use as catalysts and in manufacture of catalysts	Local exhaust ventilation; personal protective equipment
Use in chemical synthesis; use as corrosion inhibitors	Local exhaust ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If liquids or solids containing soluble chromic or chromous salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

### • Skin Exposure

If liquids or solids containing soluble chromic or chromous salts get on the skin, promptly flush the contaminated skin with water. If liquids or solids containing soluble chromic or chromous salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of soluble chromic or chromous salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

When liquids or solids containing soluble chromic or chromous salts have been swallowed give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If soluble chromic or chromous salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble chromic or chromous salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Soluble chromic or chromous salts may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chromium (as Cr)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Barborik, M.: "The Problem of Harmful Exposures to Chromium Compounds," *Industrial Medicine*, 39:5, pp. 45-47, May, 1970.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Committee on Medical and Biologic Effects of Environmental Pollutants, Division of Medical Sciences, National Research Council: *Chromium*, National Academy of Sciences, Washington, D.C., 1974.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Hamilton, A., and Hardy, H.: *Industrial Toxicology* (3rd ed.), Publishing Sciences Group, Acton, Massachusetts, 1974.
- Hueper, N. C., and Payne, W. W.: "Experimental Studies in Metal Carcinogenesis," *Archives of Environmental Health*, 5:445-462, 1962.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.
- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . Occupational Exposure to Chromic Acid*, HEW Publication No. HSM 73-11021, GPO No. 017-033-00020, U.S. Government Printing Office, Washington, D.C., 1973.
- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . Occupational Exposure to Chromium (VI)*, HEW Publication No. (NIOSH) 76-129, GPO No. 017-033-00125-1, U.S. Government Printing Office, Washington, D.C., 1975.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Pierce, J. O., and Scheel, L. D.: "Toxicity of Alloys of Chromium. I. Solubility of Chromium in Solutions of Water and Protein," *Archives of Environmental Health*, 10:870-876, 1965.

## \* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

### RESPIRATORY PROTECTION FOR SOLUBLE CHROMIC AND CHROMOUS SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m <sup>3</sup>
Particulate Concentration	
2.5 mg/m <sup>3</sup> or less	Any dust and mist respirator, except single-use.**
5 mg/m <sup>3</sup> or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume respirator or high efficiency particulate respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m <sup>3</sup> or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m <sup>3</sup> or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

\*\*If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Information in this sheet applies to workplace exposure resulting from processing, manufacturing, storing or handling and is not designed for the population at large. Any generalization beyond occupational exposures should not be made. The best industrial hygiene practice is to maintain concentrations of all chemicals at levels as low as is practical.

Chemical Names: Lead, CAS 7439-92-1; lead carbonate, CAS 598-63-0; lead chloride, CAS 7758-95-4; lead monoxide, CAS 1317-36-8; lead sulfide, CAS 1314-87-0; and others.

Trade Names: C.I. Pigment Metal 4, C.I. 77575, Lead flake, Whole lead, Litharge and others.

Uses: Tank linings, piping and other chemical reaction equipment; petroleum refining; manufacture of gasoline additives; pigments for paint; storage batteries, solder and fusible alloys; radiation shielding and others.

#### PHYSICAL INFORMATION

Appearance: Bluish white to silvery grey solid (lead metal).

Odor: None.

Behavior in Water: Insoluble.

#### HEALTH HAZARD INFORMATION

OSHA Standard: Average 8 hour exposure --  $0.05 \text{ mg/m}^3$  (lead).

NIOSH Recommended Limit: Average 10 hour day/40 hour week exposure --  $0.1 \text{ mg/m}^3$  (lead).

ACGIH Recommended Limit: Average 8 hour exposure --  $0.15 \text{ mg/m}^3$  (lead).

NOTE: Current OSHA regulations require that if an individual has a blood-lead level greater than or equal to .060 mg lead per 100 ml. blood, he must be removed from all exposures to lead and cannot return to an exposed environment until the blood level fall to .040 mg lead per 100 ml. blood or less.

#### Short Term Exposure:

Note: Lead is a cumulative poison. Increasing amounts build up in the body and eventually a point is reached where symptoms and disability may occur. Lead dust carried home on contaminated clothing can cause symptoms in other family members. Standards only protect for inhalation exposure. Extra precautions should be taken if skin exposure also occurs.

Inhalation: The effects of exposure to fumes and dusts of inorganic lead may not develop quickly. Symptoms may include decreased physical fitness, fatigue, sleep disturbance, headache, aching bones, and muscles, constipation, abdominal pains and decreased appetite. These effects are reversible and complete recovery is possible. Inhalation of large amounts of lead may lead to seizures, coma and death.

Skin: May cause irritation.

Eyes: May cause irritation.

Ingestion: See effects listed for inhalation. Ingestion of large amounts of lead may lead to seizures, coma and death.

#### Long Term Exposure:

Lead can accumulate in the body over a period of time. Therefore, long term exposures to lower levels can result in a build up of lead in the body and more severe symptoms. These may include anemia, pale skin, a blue line at the gum margin, decreased hand-grip strength, abdominal pain, severe constipation, nausea, vomiting, and paralysis of the wrist joint. Prolonged exposure may also result in kidney damage. If the nervous system is affected, usually due to very high exposures, the resulting effects include severe headache, convulsions, coma, delirium and death. In non-fatal cases, recovery is slow and not always complete. Alcohol ingestion and physical exertion may bring on symptoms. Continuous exposure can result in decreased fertility. Lead exposure of either parent before pregnancy can increase the chances of miscarriage or birth defects. Exposure of the mother during pregnancy can cause birth defects.

\*Prepared by the Bureau of Toxic Substance Assessment, New York State Department of Health.  
For an explanation of the terms and abbreviations used, see "Toxic Substances: How Toxic is Toxic" available from the New York State Department of Health.

### EMERGENCY AND FIRST AID INSTRUCTIONS

Inhalation: Move victim to fresh air. Give artificial respiration as needed. Get medical attention immediately.

Skin: Wash area with plenty of soap and water. Remove any contaminated clothing immediately.

Eyes: Rinse eyes with plenty of water for 15 minutes. Seek medical attention, if necessary.

Ingestion: If victim is conscious, give water. Seek medical attention.

Note to Physician: Whole blood lead levels, circulating plasma/erythrocyte lead concentration ratio, urine ALA, and erythrocyte protoporphyrin fluorescent microscopy may all be useful in monitoring or assessing lead exposure. Chelating agents such as edetate disodium calcium and penicillamine are generally useful in the therapy of acute lead intoxication.

### FIRE AND EXPLOSION INFORMATION

General: Not combustible. If exposed to fire, may release toxic fumes or sulfur and lead oxides.

Extinguisher: Use extinguisher appropriate to burning material. When fighting fire, wear a self-contained breathing apparatus with a full facepiece and operated in positive pressure mode.

### REACTIVITY

Conditions to Avoid: Excessive heat.

Materials to Avoid: Reacts violently with potassium.

### PROTECTIVE MEASURES

Storage and Handling: Store in an area away from heat and keep separate from potassium.

Engineering Controls: Adequate ventilation, sinks, showers and eyewash stations should be provided.

Protective Clothing (Should not be substituted for proper handling and engineering controls): Full body work clothing should be worn including bump caps or hard hats, rubber gloves, and eye protection. Employees should routinely wash their skin thoroughly and change clothing at the end of each work shift.

Protective Equipment: For levels up to 0.5 mg/m<sup>3</sup> use any dust and mist respirator, except single-use. For up to 1 mg/m<sup>3</sup> use any dust and mist respirator, except single-use or quarter mask, or any fume respirator or high efficiency particulate filter respirator. For up to 5 mg/m<sup>3</sup> use a high efficiency particulate filter respirator with a full facepiece. For up to 100 mg/m<sup>3</sup> use a powered air-purifying respirator with a high efficiency particulate filter or a Type C supplied-air respirator operated in pressure demand or other positive-pressure or continuous flow mode. For up to 200 mg/m<sup>3</sup> use a Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive-pressure mode or with a full facepiece, helmet or hood operated in continuous-flow mode. For levels greater than 200 mg/m<sup>3</sup> escape or entry into unknown concentrations use a self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive-pressure mode or a combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive-pressure or continuous flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.

Miscellaneous: No eating, drinking, or smoking in areas where the dusts or fumes of lead or its compounds are present.

### PROCEDURES FOR SPILLS AND LEAKS

Get all workers out of spill area. Put on necessary protective equipment including respirators. If spill is a solution cover with absorbent and shovel into suitable container. If spill is in powder form, vacuum whenever possible to avoid raising dust by sweeping or blowing. Place in suitable container. For final disposal contact your regional office of the New York State Department of Environmental Conservation.

more information:

Contact the Industrial Hygienist or Safety Officer at your worksite or the New York State Department of Health, Bureau of Toxic Substance Assessment, Empire State Plaza, Tower Building, Albany, New York 12237.

# Occupational Health Guideline for Inorganic Mercury

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula: Hg
- Synonyms: Quicksilver
- Appearance and odor: Silvery, mobile, odorless liquid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mercury is a ceiling level of 0.1 milligram of mercury per cubic meter of air ( $\text{mg}/\text{m}^3$ ). NIOSH has recommended that the permissible exposure limit be changed to 0.05  $\text{mg}/\text{m}^3$  averaged over an eight-hour work shift. The NIOSH Criteria Document for Inorganic Mercury should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Mercury can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may enter the body through the skin.

### • Effects of overexposure

**1. Short-term Exposure:** Inhaled mercury vapor may cause headaches, cough, chest pains, chest tightness, and difficulty in breathing. It may also cause chemical pneumonitis. In addition, it may cause soreness of the mouth, loss of teeth, nausea, and diarrhea. Liquid mercury may irritate the skin.

**2. Long-term Exposure:** Repeated or prolonged exposure to mercury liquid or vapor causes effects which develop gradually. The first effects to occur are often

fine shaking of the hands, eyelids, lips, tongue, or jaw. Other effects are allergic skin rash, headache, sores in the mouth, sore and swollen gums, loose teeth, insomnia, excess salivation, personality change, irritability, indecision, loss of memory, and intellectual deterioration.

**3. Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to mercury.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to mercury at potentially hazardous levels:

#### **1. Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of allergies or known sensitization to mercury, chronic respiratory disease, nervous system disorders, or kidney disease would be expected to be at increased risk from exposure. Examination for any signs or symptoms of unacceptable mercury absorption such as weight loss, insomnia, tremors, personality changes, or other evidence of central nervous system involvement, as well as evidence of kidney damage, should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to mercury, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Determination of mercury level in urine may be helpful in assessing extent of absorption.

**2. Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service    Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

- **Summary of toxicology**

Acute exposure to mercury at high levels causes severe respiratory irritation, digestive disturbances, and marked renal damage; chronic mercurialism, the form of intoxication most frequently caused by occupational exposure, is characterized by neurologic and psychic disturbances, anorexia, weight loss, and stomatitis. Skin absorption of inorganic mercury probably adds to the toxic effects of vapor inhalation. Intraperitoneal injection of metallic mercury in rats has produced sarcomas. Exposure of humans to mercury vapor in concentrations of 1.2 to 8.5 mg/m<sup>3</sup> causes cough, chest pain and dyspnea, leading to bronchitis and pneumonitis. Metallic mercury readily vaporizes at room temperature, and the vapor has no warning properties. At low levels, the onset of symptoms resulting from chronic exposure is insidious; fine tremors of the hands, eyelids, lips and tongue are often the presenting complaint. Coarse jerky movements and incoordination may interfere with the fine movements considered necessary for writing and eating. Psychic disturbances such as insomnia, irritability, and indecision occur; headache, excessive fatigue, anorexia, digestive disturbances, and weight loss are common; stomatitis with excessive salivation is sometimes severe; muscle weakness has been reported. Proteinuria may occur, but is relatively infrequent. Mercury has been reported to be capable of causing sensitization dermatitis. Examination of urine for mercury may be of value. There is no "critical" level of mercury in urine above or below which poisoning cannot be seen. Various observers have suggested from 0.1 to 0.5 mg of Hg/l of urine as having clinical significance. Mercury, particularly organic forms, is known to adversely affect the fetus if the mother is exposed during pregnancy.

## CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 200.6
2. Boiling point (760 mm Hg): 357 C (674 F)
3. Specific gravity (water = 1): 13.5
4. Vapor density (air = 1 at boiling point of mercury): Not applicable
5. Melting point: -39 C (-38 F)
6. Vapor pressure at 20 C (68 F): 0.0012 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.002
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with acetylene, acetylene products, or ammonia gases may form solid products that are sensitive to shock and which can initiate fires of combustible materials.
3. Hazardous decomposition products: None
4. Special precautions: Mercury can attack copper and copper alloy materials.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Mercury is odorless.

2. Eye Irritation Level: Grant states that "when mercury metal droplets are in the epithelium, rather than the corneal stroma or anterior chamber, they are extruded rapidly with little reaction, as was reported in a patient who was sprayed forcefully with metallic mercury and was observed to have many fine silvery globules beneath the epithelium of the cornea . . . ."

"Mercury metal in contact with the conjunctiva has been shown in rabbits to be absorbed and ultimately to be detectable in the urine. While in contact with the conjunctiva, metallic mercury produced no clinical signs of conjunctivitis, but histologically an inflammatory reaction has been demonstrable. External contact with mercury vapor has repeatedly been observed to induce a characteristic discoloration of the crystalline lens (mercurialentis)." Mercurialentis also is caused by systemic poisoning "from absorption of mercury vapor through the respiratory tract, the skin, and the gastrointestinal tract."

For the purposes of this guideline, mercury is not treated as an eye irritant.

3. Evaluation of Warning Properties: Mercury has no warning properties, according to the *Hygienic Guide*.

## MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of mercury. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of mercury with a three-section solid phase sampler, followed by analysis with an atomic absorption spectrophotometer. An analytical method for mercury is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may

be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid mercury.
- If employees' clothing may have become contaminated with mercury, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with mercury should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of mercury from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the mercury, the person performing the operation should be informed of mercury's hazardous properties.
- Non-impervious clothing which becomes contaminated with mercury should be removed promptly and not reworn until the mercury is removed from the clothing.

## SANITATION

- Workers subject to skin contact with liquid mercury should wash with soap or mild detergent and water any areas of the body which may have contacted mercury at the end of each work day.
- Skin that becomes contaminated with mercury should be promptly washed or showered with soap or mild detergent and water to remove any mercury.
- Eating and smoking should not be permitted in areas where mercury is handled, processed, or stored.
- Employees who handle mercury should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to mercury may occur and control methods which may be effective in each case:

### Operation

Use as a liquid cathode in electrolytic production of chlorine and caustic soda from brine

Use during manufacture and repair of industrial and medical apparatus; use during manufacture of inorganic and organic compounds for use as pesticides, antiseptics, germicides, and skin preparations, and miscellaneous applications as chemical intermediates, preservatives, and pigments

Use in preparation of amalgams for use in tooth restorations, chemical processing, and molding operations; use during manufacture of mildew-proof paints and marine antifouling agents

Use in manufacture of organic mercurials; use in manufacture of batteries, lamps, and power tubes; manufacture of tungsten-molybdenum wire and rods; use in manufacture of inorganic salts for use as catalysts in production of urethanes, vinyl chloride monomers, anthraquinone derivatives, and other miscellaneous chemicals

### Controls

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping



## Operation

Use as a chemical intermediate and in the manufacture of felt; as a flotation agent in manufacture of bowling balls; use as a laboratory reagent or as a working fluid in instruments

Use as a conductor during construction and maintenance of military and nuclear power systems, in mercury-stem boilers, and in air-rectifiers

Liberation during roasting and smelting operations

Use in manufacture of explosives; in preparation of amalgams for use in artificial jewelry

Use in manufacture of compounds for pulp and paper industry as controls for biological growths

Liberation during mining and subsequent refining of ore containing cinnabar

## Controls

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

General dilution ventilation; personal protective equipment; meticulous housekeeping

General dilution ventilation; local exhaust ventilation

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

General dilution ventilation; personal protective equipment; meticulous housekeeping

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If liquid mercury gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

### • Skin Exposure

If liquid mercury gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid mercury penetrates through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of mercury, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

When large quantities of mercury have been swallowed or mercury has been swallowed repeatedly and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If mercury is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material for reclamation using commercially available mercury vapor depressants or specialized vacuum cleaners.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Mercury as Hg," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Mercury and Its Inorganic Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1966.
- American National Standard Acceptable Concentrations - Mercury: ANSI-Z37.8-1972, American National Standards Institute, Inc., New York, 1972.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Danziger, S. J., and Possick, P. A.: "Metallic Mercury Exposure in Scientific Glassware Manufacturing Plants," *Journal of Occupational Medicine*, 15:1, pp. 15-20, 1973.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and

Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• Hunter, D.: *Diseases of Occupations* (4th ed.), Little, Brown, Boston, 1969.

• International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

• Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.

• *Mercury Poisoning*, Occupational Health Technical Information Service, California State Department of Public Health, 1963.

• National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . Occupational Exposure to Inorganic Mercury*, HEW Publication No. HSM 73-11024, GPO No. 017-033-00022, U.S. Government Printing Office, Washington, D.C., 1973.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Vostal, J. J., and Clarkson, T. W.: "Mercury as an Environmental Hazard," *Journal of Occupational Medicine*, 15:649-656, 1973.

• "Working with Mercury in Industry," *U.S. Department of Health, Education, and Welfare Pamphlet*, U.S. Government Printing Office, Washington, D.C., 1973.

## RESPIRATORY PROTECTION FOR INORGANIC MERCURY

### Condition

### Minimum Respiratory Protection\* Required Above 0.1 mg/m<sup>3</sup>

Particulate or Vapor  
Concentration

1 mg/m<sup>3</sup> or less

Any supplied-air respirator.

Any self-contained breathing apparatus.

5 mg/m<sup>3</sup> or less

Any supplied-air respirator with a full facepiece, helmet, or hood.

Any self-contained breathing apparatus with a full facepiece.

28 mg/m<sup>3</sup> or less

A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.

Greater than 28 mg/m<sup>3</sup> or  
entry and escape from  
unknown concentrations

Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.

Fire Fighting

Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

Escape

Any gas mask providing protection against mercury.

Any escape self-contained breathing apparatus.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

# Occupational Health Guideline for Selenium and Its Inorganic Compounds (as Selenium)\*

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to all selenium and its inorganic compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Selenium

- Formula: Se
- Synonyms: Selenium, metallic; selenium, elemental
- Appearance and odor: Black, gray, or red odorless solid.

### Sodium selenite

- Formula:  $\text{Na}_2\text{SeO}_3$
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

### Sodium selenate

- Formula:  $\text{Na}_2\text{SeO}_4$
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

### Selenium dioxide

- Formula:  $\text{SeO}_2$
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

### Selenium oxychloride

- Formula:  $\text{SeOCl}_2$
- Synonyms: None
- Appearance: Colorless to yellow liquid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium and its inorganic compounds is 0.2 milligram of selenium and its inorganic compounds (as selenium) per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect the body if they are inhaled, if they come in contact with the eyes or skin, or if they are swallowed. Selenium oxychloride and selenium dioxide may enter the body through the skin.

### • Effects of overexposure

*1. Short-term Exposure:* Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye," an allergy of the eyelids in which they may become puffy.

*2. Long-term Exposure:* Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen, and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service    Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

**3. Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to selenium and its inorganic compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium and its inorganic compounds at potentially hazardous levels:

**1. Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

—Urinalysis: Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Selenium causes liver damage and tumors in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

**2. Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes irritate the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/m<sup>3</sup> for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen, and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage, and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised, based upon observations in animals, but it has not been established in man. Eleven of 53 rats developed adenoma or low-grade carcinoma in cirrhotic livers, and four others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7, or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In

control rats 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1%. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea, followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/m<sup>3</sup>, while urinary levels ranged from below 0.10 to 0.43 mg/l; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred, and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide, which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

## CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Selenium**

1. Molecular weight: 78.96
2. Boiling point (760 mm Hg): 685 C (1265 F)
3. Specific gravity (water = 1): 4.45 to 4.8
4. Vapor density (air = 1 at boiling point of selenium): Not applicable
5. Melting point: 150 C (302 F)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenite**

1. Molecular weight: 173
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1
4. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
5. Melting point: 710 C (1310 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 85
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenate**

1. Molecular weight: 188.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1

4. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg

83

7. Solubility in water, g/200 g water at 20 C (68 F): 83
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Selenium dioxide**

1. Molecular weight: 110.9
2. Boiling point (760 mm Hg): 315 C (599 F) (sublimes)
3. Specific gravity (water = 1): 3.95
4. Vapor density (air = 1 at boiling point of selenium dioxide): Not applicable
5. Melting point: 340 C (644 F)
6. Vapor pressure at 20 C (68 F): 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 257

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Selenium oxychloride**

1. Molecular weight: 165.9
2. Boiling point (760 mm Hg): 176 C (349 F)
3. Specific gravity (water = 1): 2.42
4. Vapor density (air = 1 at boiling point of selenium oxychloride): 5.7
5. Melting point: 10.8 C (51 F)
6. Vapor pressure at 20 C (68 F): 0.35 mm approximately
7. Solubility in water, g/100 g water at 20 C (68 F): Decomposes

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Selenium: Data not available; sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride: Not applicable
3. Flammable limits in air, % by volume: Not applicable

4. Extinguishant: For selenium, water

• **Warning properties**

The *Documentation of TLVs* notes that "Clinton reported intense irritation of eyes, nose, and throat, followed by headache, in a group of workers briefly exposed to

high concentrations of selenium fume." The ILO reports that "persons who work in atmospheres containing selenium dioxide dust may develop a condition known among the workers as 'rose eye,' a pink allergy of the eyelids, which often become puffy. There is usually also a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctiva." The *Hygienic Information Guide* for selenium states that "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." Grant reports that both selenium dioxide and selenium sulfide can produce toxic effects on the eye. Quantitative information concerning air concentrations of selenium compounds which cause eye irritation is not available.

## MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of selenium and its inorganic compounds on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for selenium and its inorganic compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with selenium oxychloride or liquids containing selenium oxychloride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with selenium dioxide or liquids containing selenium dioxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to selenium, selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with selenium oxychloride should be removed immediately and not reworn until the selenium oxychloride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of selenium dioxide, selenium oxychloride, or liquids containing these compounds contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to selenium oxychloride, selenium dioxide, or liquids containing these compounds, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Workers subject to skin contact with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds at the end of each work day.
- Skin that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these substances should be promptly washed or showered to remove any contaminant.
- Skin that becomes contaminated with selenium oxychloride should be immediately washed or showered to remove any selenium oxychloride.
- Eating and smoking should not be permitted in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to selenium and its inorganic compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining recovery, and purification and manufacture of selenium compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls	Operation	Controls
Use in glassware industry for decolorization of fiberglass, scientific glassware, vehicular tail lights, traffic and other signal lenses, and infrared equipment; use in manufacture of electrical components in welding, transformers, semiconductors, photoelectric cells, etc.	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in manufacture of delayed action blasting caps	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photography and photocopy devices; manufacture of dyes, pigments, and colored glazes for metal etching and for printing on glass	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use as solvents in paint and varnish removers; rubber, resin, and glue solvent; use for organic synthesis in oxidation, hydrogenation, and dehydrogenation	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of lubricating oils and extreme pressure lubricants as antioxidants and detergency improvers	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in refining of copper, silver, gold, or nickel ores or during recycling of scrap metal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry for manufacture and use as vulcanization accelerators and antioxidants; use in manufacture of pharmaceuticals, fungicides, and dermatitis control	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in miscellaneous operations in manufacture of insect repellants, activators, hardeners, special ceramic materials, plasticizers, and mercury vapor detectors	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst for hardening fats for soaps, waxes, edible fats, and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use for preparation of feed additives for poultry and swine	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, parasiticides, bactericides, and herbicides for agricultural and citrus crops	Local exhaust ventilation; general dilution ventilation; personal protective equipment		
Use in manufacture of flame-proofing agents on textiles and electric cables	Local exhaust ventilation; general dilution ventilation; personal protective equipment		

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If selenium or its inorganic compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

### • Skin Exposure

If selenium or its inorganic compounds get on the skin, immediately wash the contaminated skin. If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through the clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of selenium, sodium selenite, sodium selenate, or selenium dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When selenium, sodium selenite, sodium selenate, selenium oxychloride, or selenium dioxide have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If selenium or its inorganic compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing selenium and its inorganic compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Selenium and its inorganic compounds may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Selenium Compounds (as Se)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Selenium and Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1959.

- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.

- Cerwenka, E. A., Jr., and Cooper, W. C.: "Toxicology of Selenium and Tellurium and Their Compounds," *Archives of Environmental Health*, 3:189-200, 1961.

- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

1969.

- Glover, J. R.: "Selenium and Its Industrial Toxicology," *Industrial Medicine*, 39(1):50-54, January 1970.

- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

- Halverson, A. W., et al.: "Development of Hemolytic Anemia in Rats Fed Selenite," *Toxicology and Applied Pharmacology*, 17:151-159, 1970.

- Hamilton, A., and Hardy, H.: *Industrial Toxicology* (3rd ed.), Publishing Sciences Group, Acton, Massachusetts, 1974.

- Hunter, D.: *Diseases of Occupations* (4th ed.), Little, Brown, Boston, 1969.

- *Hygienic Information Guide No. 59 - Selenium Compounds (as Se)*, Commonwealth of Pennsylvania, Department of Environmental Resources, Bureau of Occupational Health, 1971.

- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1974.

- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.

- Nelson, A. A., et al.: "Liver Tumors Following Cirrhosis Caused by Selenium in Rats," *Cancer Research*, 3:230-236, 1943.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

- Robertson, D. S. F.: "Selenium - A Possible Teratogen?," *Lancet*, 1:518-519, 1970.

- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

- Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.

## \* SPECIAL NOTE

Selenium and its inorganic compounds (as selenium) appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).



# RESPIRATORY PROTECTION FOR SELENIUM AND ITS INORGANIC COMPOUNDS (AS SELENIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m <sup>3</sup>
Particulate Concentration	
10 mg/m <sup>3</sup> or less	<p>A high efficiency particulate filter respirator with a full facepiece.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
100 mg/m <sup>3</sup> or less	<p>A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.</p> <p>A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.</p>
Greater than 100 mg/m <sup>3</sup> or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p>
Escape	<p>A high efficiency particulate filter respirator with a full facepiece.</p> <p>Any escape self-contained breathing apparatus with a full facepiece.</p>

\*Only NIOSH-approved or MSHA-approved equipment should be used.

# Occupational Health Guideline for Selenium Hexafluoride

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula:  $\text{SeF}_6$
- Synonyms: None
- Appearance: Colorless gas.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium hexafluoride is 0.05 part of selenium hexafluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of selenium hexafluoride per cubic meter of air ( $\text{mg}/\text{m}^3$ ).

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Selenium hexafluoride can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

### • Effects of overexposure

Animal experiments have shown selenium hexafluoride to be a severe respiratory irritant which has produced severe breathing difficulties. These breathing difficulties may be delayed in onset.

### • Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to selenium hexafluoride.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to selenium hexafluoride at potentially hazardous levels:

#### 1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Selenium hexafluoride causes lung damage in animals. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Selenium hexafluoride is a severe pulmonary irritant in animals. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or when signs and symptoms of respiratory disease occur.

### • Summary of toxicology

Selenium hexafluoride gas is a severe respiratory irritant in animals. Exposure of four animal species to 10 ppm for 4 hours was fatal; 5 ppm for 4 hours was not fatal but caused pulmonary edema, while 1 ppm produced no effects. Animals exposed to 5 ppm for 1 hour daily for 5 days developed signs of pulmonary injury; 1 ppm for the same time period caused no detectable effects.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 193
2. Boiling point (760 mm Hg):  $-35^\circ\text{C}$  ( $-31^\circ\text{F}$ )
3. Specific gravity (water = 1): 2.3 (liquid)
4. Vapor density (air = 1 at boiling point of selenium hexafluoride): 6.7
5. Melting point:  $-39^\circ\text{C}$  ( $-38^\circ\text{F}$ )
6. Vapor pressure at  $20^\circ\text{C}$  ( $68^\circ\text{F}$ ): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at  $20^\circ\text{C}$  ( $68^\circ\text{F}$ ): Insoluble; reacts slowly

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None

2. Incompatibilities: None

3. Hazardous decomposition products: Data not available

4. Special precautions: None

- **Flammability**

1. Not combustible

2. See 29 CFR 1910.101 for specific regulations on storage of compressed gas cylinders.

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of selenium hexafluoride.

2. Eye Irritation Level: There is no indication in the available toxicological information that selenium hexafluoride produces eye irritation. Concerning fluorides, however, Grant states that "irritation of the eyes and nose has been reported when fluoride concentration has reached 5 mg/m<sup>3</sup> of air."

3. Evaluation of Warning Properties: Since no quantitative information is available relating warning properties to air concentrations of selenium hexafluoride, this compound is treated as a material with poor warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure selenium hexafluoride may be used. An analytical method for selenium hexafluoride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used

when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to selenium hexafluoride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a gaseous electric insulator	Process enclosure; local exhaust ventilation; personal protective equipment
Use during production of selenium hydroxide and hydrofluoric acid, selenium and nitrogen	Process enclosure; local exhaust ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of selenium hexafluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.
- If selenium hexafluoride is leaked, the following steps should be taken:

1. Ventilate area of leak.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Selenium Hexafluoride," *Documentation of*

*the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

- American Industrial Hygiene Association: "Selenium and Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1959.

- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

## RESPIRATORY PROTECTION FOR SELENIUM HEXAFLUORIDE

Condition	Minimum Respiratory Protection* Required Above 0.05 ppm
Gas Concentration	
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2.5 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against selenium hexafluoride. Any escape self-contained breathing apparatus.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

# Occupational Health Guideline for Silver Metal and Soluble Silver Compounds

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## APPLICABILITY

The general guidelines contained in this document apply to metallic silver and all soluble silver compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Silver, metallic

- Formula: Ag
- Synonyms: None
- Appearance and odor: Characteristic white metallic solid with no odor.

### Silver nitrate

- Formula:  $\text{AgNO}_3$
- Synonyms: Argerol; lunar caustic
- Appearance and odor: Colorless and odorless solid which may become gray on storage.

### Silver fluoride

- Formula:  $\text{AgF}$
- Synonyms: None
- Appearance and odor: Yellow-white, odorless solid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for silver metal and soluble silver compounds is 0.01 milligram of silver metal and soluble silver compounds per cubic meter of air ( $\text{mg}/\text{m}^3$ ) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for silver metal and soluble silver compounds from 0.01  $\text{mg}/\text{m}^3$  to 0.1  $\text{mg}/\text{m}^3$ .

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Silver or soluble silver compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

### • Effects of overexposure

Silver or soluble silver compounds can cause discoloration or blue-gray darkening of the eyes, nose, throat, and skin. Silver nitrate is strongly corrosive and can cause burns and permanent damage to the eyes and can burn the skin.

### • Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to silver metal or soluble silver compounds.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to silver metal and soluble silver compounds at potentially hazardous levels:

#### 1. Initial Medical Examination:

—Examination of the nasal septum, eyes, and skin for evidence of pigmentation: The purpose is to establish a baseline for future observations of silver deposition in tissues.

#### 2. Periodic Medical Examination: The aforementioned

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

The dust of silver and its soluble compounds cause argyria, the local or generalized impregnation of the mucous membranes, skin, and eyes with silver. Localized argyria occurs in the skin, eyes, nasal septum and throat, where gray-blue patches of pigmentation are formed without evidence of tissue reaction. Generalized argyria is recognized by the widespread pigmentation of the skin and may be seen first in the conjunctiva, with some localization in the inner canthus. Argyrosis of the respiratory tract has been described in two workers involved in the manufacture of silver nitrate; their only symptom was mild, chronic bronchitis; bronchoscopy revealed tracheobronchial pigmentation; biopsy of the nasal mucous membrane showed silver deposition in the subepithelial area. A total body burden from 1 to 5 g of silver will lead to generalized argyria. Silver, once deposited in the body, is poorly excreted in the urine in amounts detectable by spectrochemical methods. Silver nitrate (lunar caustic) may cause irritation, ulcers, and discoloration of skin; if ingested, it may cause abdominal pain and gastroenteritis.

## CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Silver, metallic**

1. Molecular weight: 107.9
2. Boiling point (760 mm Hg): 2200 C (3992 F)
3. Specific gravity (water = 1): 10.4
4. Vapor density (air = 1 at boiling point of metallic silver): Not applicable
5. Melting point: 966 C (1771 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Silver nitrate**

1. Molecular weight: 169.9
2. Boiling point (760 mm Hg): 444 C (831 F) (decomposes)
3. Specific gravity (water = 1): 4.4
4. Vapor density (air = 1 at boiling point of silver nitrate): Not applicable
5. Melting point: 209 C (408 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F):

245  
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Silver fluoride**

1. Molecular weight: 126.9
2. Boiling point (760 mm Hg): 1159 C (2119 F) (approximately)
3. Specific gravity (water = 1): 5.8
4. Vapor density (air = 1 at boiling point of silver fluoride): Not applicable

5. Melting point: 435 C (815 F)

6. Vapor pressure at 20 C (68 F): Negligible

7. Solubility in water, g/100 g water at 20 C (68 F): 64

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact of metallic silver and soluble silver compounds with acetylene may cause formation of silver acetylide that is sensitive to shock. Contact with ammonia may cause formation of compounds that are explosive when dry. Contact with strong hydrogen peroxide solutions will cause violent decomposition to oxygen gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when some soluble silver compounds decompose.

4. Special precautions: Soluble silver compounds will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Most soluble silver compounds are not combustible. However, silver nitrate is a strong oxidizing material capable of increasing the flammability of combustible, organic, or other readily oxidizable materials. The following soluble silver compounds are explosives and should be stored and handled in accordance with 29 CFR 1910.109: silver acetylide, silver azide, silver fulminate, silver oxalate mixtures, silver styphnate, silver tartarate mixtures, and silver tetrazene.

• **Warning properties**

According to Stecher "many silver salts are irritating . . . to mucous membranes." Grant notes that many simple silver salts and silver ammonium compounds are injurious to the eye. According to Grant, "a great many reports have been published describing argyrosis of the eye, either from local contact with silver compounds or as a part of a generalized argyrosis from systemic absorption of silver or its compounds." Since there are inadequate data to assess the effects on the eye at or near the permissible exposure limit, for the purposes of this guideline, silver metal and soluble silver compounds are considered to have poor warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for silver metal and soluble silver

compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with powdered metallic silver or solids or liquids containing soluble silver compounds, where skin contact may occur.
- If employees' clothing may have become contaminated with solids or liquids containing soluble silver compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with metallic silver or soluble silver compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substances from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the substances, the person performing the operation should be informed of substances' hazardous properties.
- Non-impervious clothing which becomes contaminated with metallic silver or soluble silver compounds should be removed promptly and not reworn until the metallic silver or soluble silver compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of powdered metallic silver or solids or liquids containing soluble silver compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to silver nitrate or solutions containing 5 percent or more silver nitrate by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Skin that becomes contaminated with metallic silver or soluble silver compounds should be promptly

washed or showered to remove any metallic silver or soluble silver compounds.

- Eating and smoking should not be permitted in areas where metallic silver or solids or liquids containing soluble silver compounds are handled, processed, or stored.
- Employees who handle powdered metallic silver or solids or liquids containing soluble silver compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to silver metal and soluble silver compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining and purification from ore; during refining from secondary sources	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of silver nitrate for use in photography, mirrors, plating, inks, dyes, and porcelain; and as germicides, antiseptics, caustics, and analytical reagents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of silver salts as catalysts in oxidation-reduction and polymerization reactions; in chemical synthesis; in glass manufacture, in silver-plating, in photography, as laboratory reagents, and in medicine	Process enclosure; local exhaust ventilation; personal protective equipment

## Operation

Liberation from manufacture and casting of alloys; during fabrication of silver metal, alloys, and bi-metals for electrical uses; and during electroplating operations and fabrication of solders and brazing alloys; during manufacture and use of photographic chemicals and materials; during manufacture of mirrors, and during manufacture of silver powder pigments and paints

Use during manufacture of silver powder pigments and paints; during manufacture of mirrors; during manufacture of photographic chemicals and materials

## Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

Local exhaust ventilation; general dilution ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If powdered metallic silver or solids or liquids containing soluble silver compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

### • Skin Exposure

If powdered metallic silver or solids or liquids containing soluble silver compounds get on the skin, flush the contaminated skin with water. If powdered metallic silver or solids or liquids containing soluble silver compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention. Other silver compounds should be removed by promptly flushing the skin with water.

### • Breathing

If a person breathes in large amounts of silver metal or soluble silver compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

If silver nitrate or other corrosive soluble silver compounds have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the silver nitrate or other corrosive silver compounds. Do not attempt to make the exposed person vomit. Get medical attention immediately. When non-corrosive soluble silver compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If powdered silver metal or soluble silver compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing silver metal or soluble silver compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Silver metal and soluble silver compounds may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

• American Conference of Governmental Industrial Hygienists: "Silver," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.

• Buckley, W. R., et al.: "Localized Argyria. II. Clinical Nature of the Silver Containing Particles," *Archives of Dermatology*, 92:697-705, 1965.

• Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.

• Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.



- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Hunter, D.: *Diseases of Occupations* (4th ed.), Little, Brown, Boston, 1969.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- Kirk, R., and Othmer, D.: *Encyclopedia of Chemical Technology* (2nd ed.), Interscience, New York, 1968.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.
- *Survey of Compounds Which Have Been Tested for Carcinogenic Activity*, U.S. Public Health Service Publication No. 149, Original, Supplements 1 and 2, 1961-1967, 1968-1969, and 1970-1971.

## RESPIRATORY PROTECTION FOR SILVER METAL AND SOLUBLE SILVER COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 0.01 mg/m <sup>3</sup>
Particulate Concentration	
0.5 mg/m <sup>3</sup> or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m <sup>3</sup> or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
20 mg/m <sup>3</sup> or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m <sup>3</sup> or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.  A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

\*Only NIOSH-approved or MSHA-approved equipment should be used.

APPENDIX B-II

HEAT AND STRESS CASUALTY PREVENTION PLAN

## A. Identification and Treatment

### 1) Heat Exhaustion

- a) Symptoms: Usually begins with muscular weakness, dizziness, nausea, and a staggering gait. Vomiting is frequent. The bowels may move involuntarily. The victim is very pale, his skin is clammy, and he may perspire profusely. The pulse is weak and fast, his breathing is shallow. He may faint unless he lies down. This may pass, but sometimes it remains and death could occur.
- b) First-Aid: Immediately remove the victim to the Decontamination Reduction Zone in a shady or cool area with good air circulation. Remove all protective outer wear. Call a physician. Treat the victim for shock. (Make him lie down, raise his feet 6-12 inches, and keep him warm but loosen all clothing.) If the victim is conscious, it may be helpful to give him sips of a salt water solution (1 teaspoon of salt to 1 glass of water). Transport victim to a medical facility.

### 2) Heat Stroke

- a) Symptoms: This is the most serious of heat casualties due to the fact that the body excessively overheats. Body temperatures often are between 107°-110°F. First there is often pain in the head, dizziness, nausea, oppression, and a dryness of the skin and mouth. Unconsciousness follows quickly and death is imminent if exposure continues. The attack will usually occur suddenly.
- b) First-Aid: Immediately evacuate the victim to a cool and shady area in the Decontamination Reduction Zone.

Removal all protective outer wear and all personal clothing. Lay him on his back with the head and shoulders slightly elevated. It is imperative that the body temperature be lowered immediately. This can be accomplished by applying cold wet towels, ice bags, etc., to the head. Sponge off the bare skin with cool water or rubbing alcohol, if available, or even place him in a tub of cool water. The main objective is to cool him without chilling him. Give no stimulants. Transport the victim to a medical facility as soon as possible.

B. Prevention of Heat Stress

- 1) One of the major causes of heat casualties is the depletion of body fluids. On the site there will be plenty of fluids available. Personnel should replace water and salts loss from sweating. Salts can be replaced by either a 0.1% salt solution, more heavily salted foods, or commercial mixes such as Gatorade. The commercial mixes are advised for personnel on low sodium diets.
- 2) A work schedule will be established so that the majority of the work day will be during the morning hours of the day before ambient air temperature levels reach their highs.

- 3) A work/rest guideline will be implemented for personnel required to wear Level B protection, if this situation arises. This guideline is as follows:

<u>Ambient Temperatures</u>	<u>Maximum Wearing Time</u>
Above 90°F	1/2 hour
80°-90°F	1 hour
70°-80°F	2 hours
60°-70°F	3 hours
50°-60°F	4 hours
40°-50°F	5 hours
30°-40°F	6 hours
Below 30°F	8 hours

A sufficient period will be allowed for personnel to "cool down". This may require shifts of workers during operations.

APPENDIX C

WELL RECORDS AND DRILLING LOGS

## NUS WELL RECORD

Project: Hukill Chemical  
Well No.: G-2  
Coordinates: See Figure 1  
On-Site Geologist: D. Wallace  
Elevation (top of pipe): 979.29  
Elevation (land surface): 975.87  
Elevation (water table): 953.38  
Date Measured: 9/15/82  
Status of Well: Complete

## DRILLING

Drilling Started: 9/13/82  
Drilling Completed: 9/14/82  
Drilling Company: Triggs & Assoc.  
Registration No.: None  
Permit No.: None Needed  
Name of Driller: Harry Grasser  
Type of Rig: Rotary (Hollow stem)  
Drilling Fluid: None

## HOLE DATA

Hole Diameter: 7 in.  
Thickness of Overburden: 28 ft.  
Depth Drilled in Rock: 5 ft.  
Total Depth of Hole: 33 ft.

## DEVELOPMENT

Method: Surging with air  
Rate of Flow: No removal  
Length of Time: 15 min.

## CASING

Type: 304 Stainless Steel (Sch. 5)  
Diameter: 2 in. ID  
Length: ~ 36.16 ft. (Total)  
Type of Joint: Threaded (flush)  
Screen Slot: #7 (0.007 in.)  
Screen Length: 10 ft.  
Screen Setting: 22.5 ft. to 32.5 ft.  
Stickup: 41.05 in.

GRAVEL

Type: Silica  
Size: Pea gravel with some sand  
Volume: ~ 20 gal.  
Depth: 21 ft to 33 ft.

GROUT

Type: Bentonite (Powder)  
Method: Poured  
Volume: ~ 400 lbs.  
Depth: 2 ft. to 21 ft.

BACKFILL

Type: None (see above)  
Cement Collar: 2 ft.

## COMMENTS

Perm. Test - 23-25 ft. - Bottom  
WL - 9/14 - 12:30am - 25.95 ft.  
WL - 9/15 - 8:40am - 25.91 ft.

# DRILLING LOG

<u>Depth</u>		<u>Formation</u>
<u>From</u>	<u>To</u>	<u>Description</u>
0 - 13 ft.		Fill - Black silty clay - Pebbles and cinders
13 ft. - 15 ft.		Gold sand (May be foundry sand)
15 ft. - 24 ft.		Fill - Black silty clay as above
24 ft. - 28 ft.		Brown silty clay - Some pebbles - Laminated
26.5 ft.		Water (Good-sized seep)
28 ft. - 30 ft.		Highly weathered greenish gray shale
30 ft. - 33 ft.		Shale - Greenish gray - Fracture well defined -
		Poorly cemented
33 ft.		BOH

## NUS WELL RECORD

Project: Hukill Chemical  
 Well No.: G-3  
 Coordinates: See Figure 1  
 On-Site Geologist: D. Wallace  
 Elevation (top of pipe): 979.53  
 Elevation (land surface): 977.03  
 Elevation (water table): 954.45  
 Date Measured: 9/15/82  
 Status of Well: Complete

### DRILLING

Drilling Started: 9/13/82  
 Drilling Completed: 9/13/82  
 Drilling Company: Triggs & Assoc.  
 Registration No.: None  
 Permit No.: None Needed  
 Name of Driller: Harry Grasser  
 Type of Rig: Rotary (Hollow stem)  
 Drilling Fluid: None

### HOLE DATA

Hole Diameter: 7 in.  
 Thickness of Overburden: 28 ft.  
 Depth Drilled in Rock: 14 ft.  
 Total Depth of Hole: 42 ft.

### DEVELOPMENT

Method: Surging with air  
 Rate of Flow: 5 min. recovery  
 Length of Time: 25 min.  
 Strong methane smell

### CASING

Type: 304 Stainless Steel (Sch. 5)  
 Diameter: 2 in. ID  
 Length: ~ 44.16 ft. (Total)  
 Type of Joint: Threaded (flush)  
 Screen Slot: #7 (0.007 in.)  
 Screen Length: 10 ft.  
 Screen Setting: 31.5 ft. to 41.5 ft.  
 Stickup: 30.05 in.

### GRAVEL

Type: Silica  
 Size: Pea gravel with some sand  
 Volume: ~ 25 gal.  
 Depth: 24 ft. to 42 ft.

### GROUT

Type: Bentonite (Powder)  
 Method: Poured  
 Volume: ~ 300 lbs.  
 Depth: 2 ft. to 24 ft.

### BACKFILL

Type: None (see above)  
 Cement Collar: 2 ft.

### COMMENTS

Perm. Test - 18.5 ft - 20 ft. - Top  
 and 23.5 - 25 ft. Bottom  
 WL - 9/14 - 9:45am - 25.08 ft.  
 WL - 9/15 - 8:30am - 25.08 ft.

## DRILLING LOG

Depth	Formation
From      To	Description
0 - 15 ft	Fill - Silty clay - Upper layer black, followed by rust, then brown - Some roots and cinders
15 ft. - 15.5 ft.	Residual grass zone - black but still distinguishable - Damp
15.5 ft. - 24 ft.	Greenish gray silty clay with shale fragments and wood chips
24 ft. - 28.5 ft.	Black clay - Organic looking with wood chips
28 ft.	Water (small seep)
28.5 ft. - 30 ft.	Highly weathered greenish gray shale
30 ft. - 35 ft.	Shale - Greenish gray - Poorly cemented
35 ft. - 42 ft.	Shale - Greenish gray - Well cemented
42 ft.	BOH



**NUS WELL RECORD**

Project: Hukill Chemical  
Well No.: G-4  
Coordinates: See Figure 1  
On-Site Geologist: D. Wallace  
Elevation (top of pipe): 980.55  
Elevation (land surface): 979.17  
Elevation (water table): 970.55  
Date Measured: 9/15/82  
Status of Well: Complete

## DRILLING

Drilling Started: 9/14/82  
Drilling Completed: 9/14/82  
Drilling Company: Triggs & Assoc.  
Registration No.: None  
Permit No.: None Needed  
Name of Driller: Harry Grasser  
Type of Rig: Rotary (Hollow stem)  
Drilling Fluid: None

## HOLE DATA

Hole Diameter: 7 in.  
Thickness of Overburden: 8.5 ft.  
Depth Drilled in Rock: 9.5 ft.  
Total Depth of Hole: 18 ft.

## DEVELOPMENT

Method: Surging with air  
Rate of Flow: 5 min. recovery  
Length of Time: 15 min.

## CASING

Type: 304 Stainless Steel (Sch. 5)  
Diameter: 2 in. ID  
Length: ~ 19.33 ft. (Total)  
Type of Joint: Threaded (flush)  
Screen Slot: #7 (0.007 in.)  
Screen Length: 10 ft.  
Screen Setting: 7.5 ft. to 17.5 ft.  
Stickup: 16.55 in.

GRAVEL

Type: Silica  
Size: Pea gravel with some sand  
Volume: ~ 18 gal.  
Depth: 6 ft. to 18 ft.

GROUT

Type: Bentonite (Powdered)  
Method: Poured  
Volume: ~ 200 lbs.  
Depth: 2 ft. to 6 ft.

BACKFILL

Type: None (see above)  
Cement Collar: 2 ft.

## COMMENTS

Perm. Test - 3.5 - 5 ft. - Bottom  
WL - 9/15 - 8:15am - 10.0 ft.

# DRILLING LOG

[illegible]

HUKILL CHEMICAL CORPORATION  
BEDFORD, OHIO

---

PLAN FOR DETERMINING  
THE EXTENT OF  
POTENTIAL CONTAMINATION

2-45  
DRAFT COPY

---

PROJECT #495-1  
FEBRUARY 1985

---

EDER ASSOCIATES  
CONSULTING ENGINEERS, P.C.  
85 Forest Avenue  
Locust Valley, New York 11560



eder associates  
consulting engineers, p.c.

February 27, 1985  
File #495-1

Mr. Ron Lillich  
Waste Management Branch  
Technical, Permits and Compliance Section  
United States Environmental Protection Agency  
Region V  
230 South Dearborn  
12th Floor  
Chicago, Illinois 60604

Re: Hukill Chemical Corporation - Bedford, Ohio  
EPA ID No. OHD 001926740

Dear Mr. Lillich:

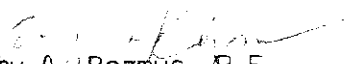
We are pleased to submit three draft copies of our engineering report entitled "Plan for Determining the Extent of Potential Contamination" for your review. This report is submitted pursuant to the Compliance Order dated December 27, 1984 and subsequent directives by the Environmental Protection Agency (EPA).

The Plan presents the work that will be conducted to: determine the nature and extent of potential contamination due to storage operations in the tank farm; determine the need for corrective actions; and select and implement the EPA approved corrective action.

If you have any questions, please do not hesitate to call.

Very truly yours,

EDER ASSOCIATES CONSULTING ENGINEERS, P.C.

  
Gary A. Rozmus, P.E.  
Vice President

GAR/nf

85 FOREST AVENUE • LOCUST VALLEY, NEW YORK 11560 • (516) 671-8440

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JOHN MCGUIRE, P.E. • JORGE MOLINA, ING. • WILLIAM J. CUNNINGHAM, P.E. • VINCENT J. FRISINA, P.E.

TABLE OF CONTENTS

<u>Description</u>	<u>Page</u>
LETTER OF TRANSMITTAL	
I. INTRODUCTION	1
- Purpose	1
- Scope	1
II. TASK 1 - BACKGROUND INFORMATION	3
III. TASK 2 - SITE INVESTIGATION	4
- 2.1 - Introduction	4
- 2.2 - Groundwater Monitoring	4
- 2.3 - Soil Analyses	7
- 2.4 - Summary of Site Investigation	11
IV. TASK 3 - REPORT OF SITE INVESTIGATION	14
V. TASK 4 - REVIEW OF ALTERNATIVE CORRECTIVE ACTIONS	16
- 4.1 - Initial Screening of Alternatives	16
- 4.2 - Detailed Analysis of Alternatives	16
- 4.3 - Preliminary Report	17
VI. TASK 5 - CONCEPTUAL DESIGN OF SELECTED ALTERNATIVE	18
VII. TASK 6 - CORRECTIVE ACTION STUDY REPORT	19
VIII. IMPLEMENTATION SCHEDULE	20
APPENDICES	

LIST OF TABLES

<u>No.</u>	<u>Description</u>	<u>Page</u>
1	Summary of Sample Types and Chemical Analyses	12
2	Implementation Schedule	21

LIST OF FIGURES

<u>No.</u>	<u>Description</u>	<u>Page</u>
1	Site Plan	5
2	Typical Shallow Monitoring Well	8
3	Typical Deep Monitoring Well	9
4	Soil Samples in & Around Tank Farm	10

## I. INTRODUCTION

### Purpose

Hukill Chemical Corporation (HCC) owns and operates a chemical processing facility located at 7013 Krick Road, Bedford, Ohio. The Company operates a tank farm located on the north side of the facility. The tank farm is used for the storage of spent and reclaimed solvents. The United States Environmental Protection Agency (EPA), Region V, is requiring HCC to conduct an investigation to: determine the nature and extent of potential contamination due to storage operations in the tank farm; determine the need for corrective actions to eliminate potential threats to the environment; and select and implement the EPA approved corrective action.

### Scope

This investigation will consist of six tasks:

Task 1: Background Information

Task 2: Site Investigation

Task 3: Report of Site Investigation

Task 4: Review of Alternative Corrective Actions

Task 5: Conceptual Design of Selected Alternative

Task 6: Corrective Action Study Report

This report will detail the work to be conducted during Tasks 1 through 6.

A plan for corrective action will be determined, if required, at the conclusion of Task 6. At such time, HCC will implement the approved plan, if required, in accordance with the approved implementation schedule.

## II. TASK 1 - BACKGROUND INFORMATION

Task 1 will involve obtaining background information pertinent to the HCC site. The information that will be gathered will include: well logs of existing monitoring wells; and hydrogeological and geological data, including information pertaining to groundwater at the site. Existing sampling data will be obtained and a list of materials stored in the tank farm, both presently and in the past, will be assembled.

The background information will be utilized in the site investigation to identify potential contaminants, areas of contamination, and the appropriate means for determining the extent of potential contamination.



### III. TASK 2 - SITE INVESTIGATION

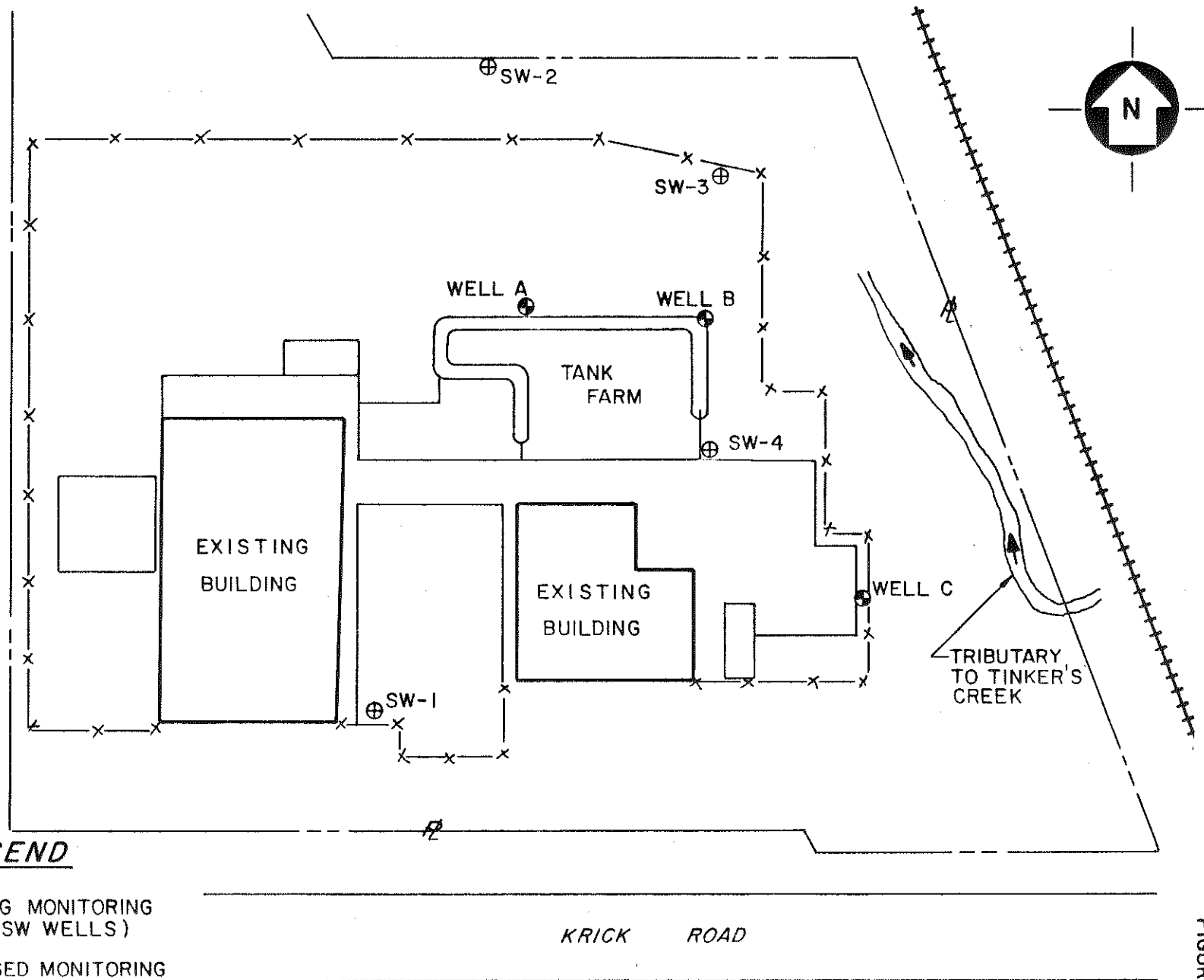
#### 2.1 - Introduction

A site investigation in and around the area of the tank farm at the HCC facility will be conducted to characterize the site and its actual or potential hazard, if any, to public health and the environment. The site investigation will result in data to assist in assessing preliminary corrective action alternatives and to evaluate alternatives during the later stages of this study. The investigation will include: the installation of additional groundwater monitoring wells and groundwater analyses; and soil sampling and analyses at various locations in and around the tank farm. The work required for this investigation is discussed in the following sections.

#### 2.2 - Groundwater Monitoring

The location of existing and proposed groundwater monitoring wells is shown in Figure 1, the site plan of the facility. The proposed wells are strategically placed in order to determine whether potential contaminants have entered the groundwater, and if so to determine the concentrations and extent of contaminants. Figure 1 shows the installation of three new monitoring wells. Each of these wells will be shallow wells. Shallow wells will intercept groundwater flow in the upper layers consisting of weathered shale.

Groundwater flow direction at the site is to the north and east towards the tributary to Tinkers Creek, shown in Figure 1. Monitoring wells A and B will be located immediately outside of the earthen berm on the north side of the tank farm. These wells will assist in detecting the presence of contaminants in the groundwater flowing to the north and northeast. Monitoring well C will be located along the east property line of the facility. This well will assist in detecting the presence of contaminants in the groundwater flowing to the east.



**LEGEND**

- ⊕ EXISTING MONITORING WELL (SW WELLS)
- PROPOSED MONITORING WELL

**SITE PLAN**

FIGURE N° 1

between the boring hole and the well casing. A locking cap will be placed on the top of the well casing. In addition, a concrete pad will be poured around the well casing at grade to prevent runoff from entering the space between the borehole and the well casing. A typical shallow well installation is shown in Figure 2. Shallow wells will be installed using a hollow stem auger.

A deep well will be installed at the facility. The location of the deep well will be determined by the shallow monitoring well showing the highest level of contamination if any is found to be occurring. The deep well will extend into shale bedrock. The well installation will include an inner four (4) inch PVC well casing and an outer six (6) inch black steel well casing. The annular space between the six (6) inch casing and the boring will be grouted with a cement/bentonite grout mixture. A well screen is not required for the deep well. This deep well design will minimize the potential of cross-contamination between groundwater flowing in the upper permeable materials and deeper impermeable layers. A typical deep well is shown in Figure 3. A locking cap will be placed on top of the well casing and a concrete pad will be poured around the well casing at grade.

### 2.3 Soil Analyses

Surface and subsurface soil samples will be collected in the tank farm and around the tank farm area. The locations of the borings required for soil samples are shown in Figure 4. Samples will be collected using a split spoon sampler. A sample will be obtained at the ground surface and at three (3) foot intervals thereafter. Soil samples will also be collected during the drilling of the three (3) monitoring wells. These samples will be collected at three (3) foot intervals.

All soil samples that are collected will be analyzed in the field for total VOC using a portable organic volatiles analyzer (OVA). The results of the OVA will be used to determine the required depth of the soil borings and the specific soil samples that will be subject to the

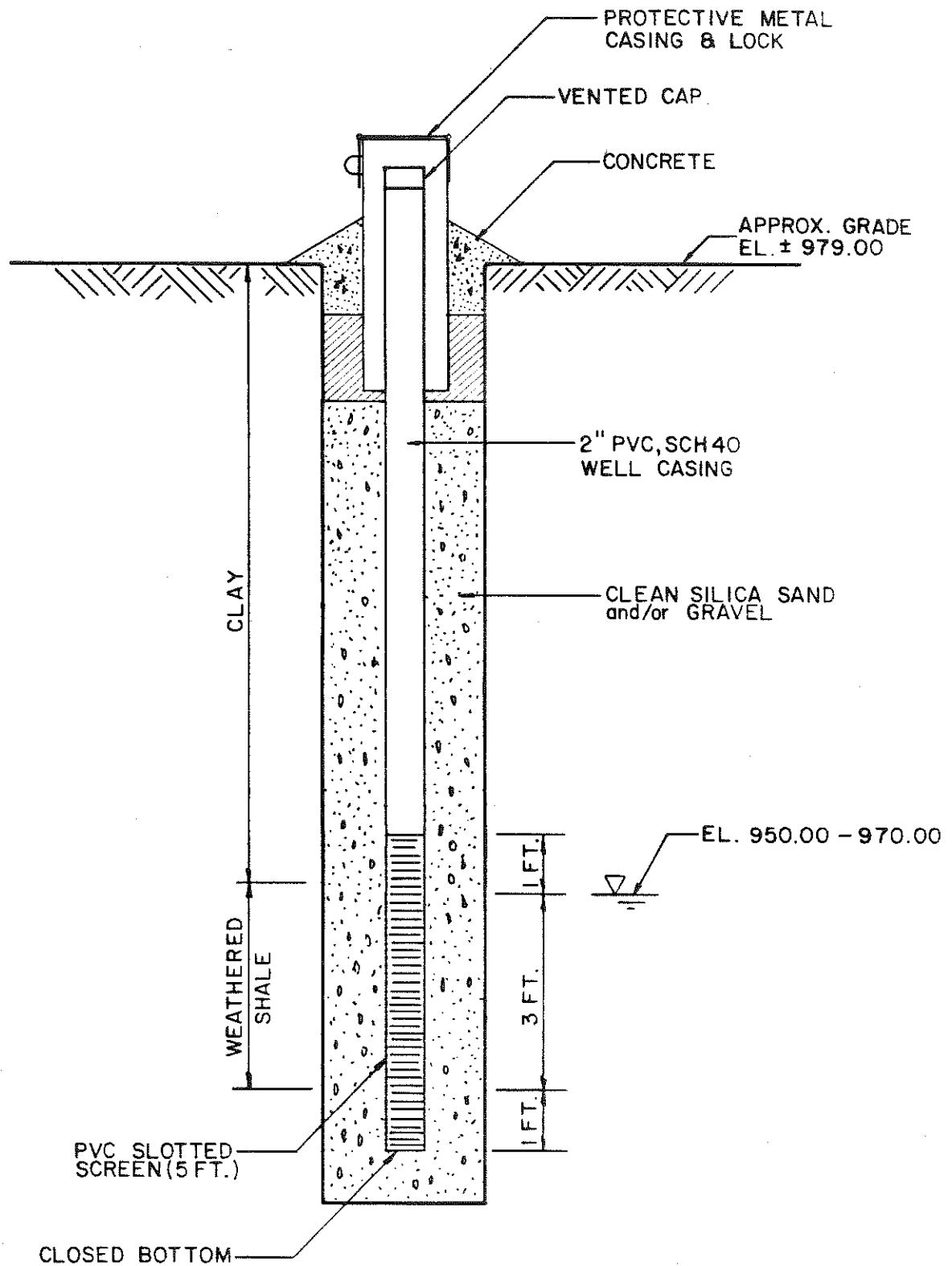
Groundwater samples will be collected from all new and existing wells. Samples will be appropriately handled, filtered and preserved prior to analyses, in accordance with the projects Quality Assurance Program Plan (QAPP) appended to this report. The parameters that will be analyzed are listed in Table 1 in Section 2.4. If contaminants are identified in the groundwater samples, a fourth, deep well (Well D) will be installed near the shallow well showing the highest concentration of contaminants. The deep well will intercept groundwater flow in the shale bedrock layer and will assist in determining the vertical extent of contamination. The installation of additional monitoring wells may be required if contamination is found to be occurring and the installed wells do not provide sufficient information to determine its extent.

Protocols for drilling, sampling and chemical analyses of the groundwater are discussed and detailed in the QAPP. Removal of water in the shallow wells before sampling will be accomplished using bailers in the shallow wells and using a displacement type pump in the deep well, if required. Samples from all wells will be collected using a bailer. Bailed water will be stored on-site until the analyses have been completed. Final disposition of bailed water will be determined upon review of sample analyses.

The results of the sampling analyses of the new and existing downgradient wells will be compared to the results of analyses from the existing upgradient well. The existing upgradient well is identified as SW-1 in Figure 1. A VOC scan will be performed on samples from the upgradient and the downgradient wells. If comparison of the VOC scans indicates that the upgradient well does not adequately monitor the quality of groundwater flowing to the HCC facility, then the installation of an additional upgradient well may be required.

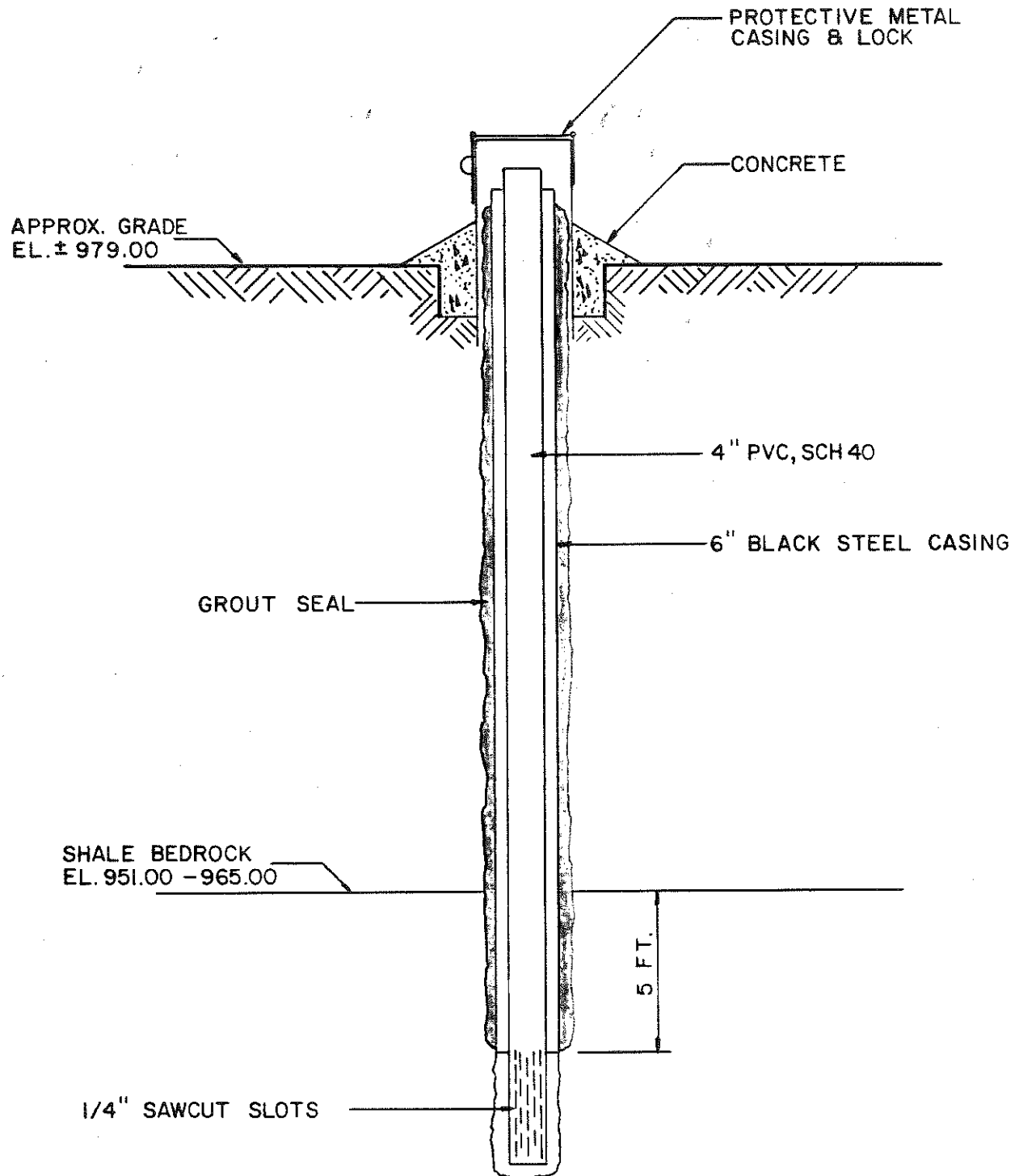
Monitoring wells A, B and C will be constructed of two (2) inch diameter PVC casing. Each well will be screened with five (5) feet of ten (10) slot (0.010 inch) screen. A bentonite seal will be placed

FIGURE Nº 2



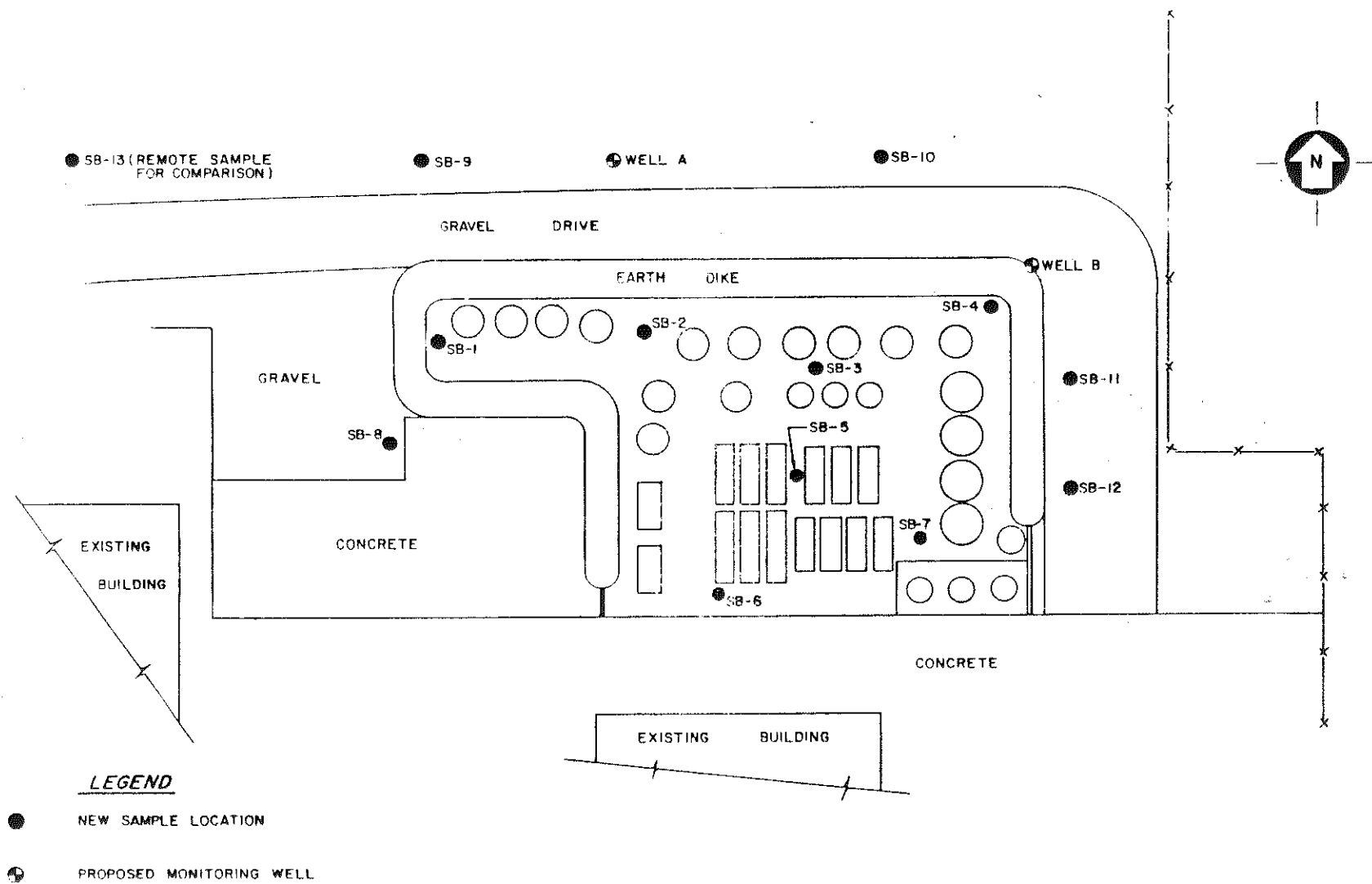
## TYPICAL SHALLOW MONITORING WELL

FIGURE N° 3



## TYPICAL DEEP MONITORING WELL

FIGURE Nº 4



# SOIL SAMPLES IN & AROUND TANK FARM

chemical analyses listed in Table 1 of Section 2.4. Soil boring No. SB-13 will be taken in an area remote to the tank farm. This sample will be considered to be clean soil for comparison to all soil samples. The sampling and chemical analyses protocols for the soil samples are discussed in the QAPP, which is appended to this report. Additional soil samples may be required if contamination is found to be occurring and the proposed soil borings do not provide sufficient information to determine its extent.

#### 2.4 Summary of Site Investigation

Table 1 presents a summary of all the chemical analyses that will be conducted for groundwater and soil samples. Protocols for sampling and analyzing that are presented in the QAPP will be strictly followed in order to avoid contamination of the samples, to ensure the accuracy of the results and to have the results represent the actual conditions of the site. Strict chain-of-custody procedures will be followed. These procedures are discussed in detail in the QAPP, which is appended to this report.

Eder Associates Consulting Engineers, P.C. (EA) will supervise all site investigation work, including the drilling of additional groundwater monitoring wells. EA will also conduct a sampling program in accordance with the established protocols.

All chemical analyses will be conducted by an outside EPA contract laboratory. All laboratory analyses will be conducted in a manner that follows the established protocols.

The results from the site investigation will be used to assess the potential hazards, if any, to health or the environment at the HCC site. This assessment will be used to determine a recommended corrective action to alleviate the potential problem, if any are found to exist.



HUKILL CHEMICAL CORPORATION  
BEDFORD, OHIO

TABLE 1

SUMMARY OF SAMPLE TYPES AND CHEMICAL ANALYSES

	<u>Groundwater</u>	<u>Soil</u>
Acetone	X	X
Benzene	X	X
Methyl Ethyl Ketone	X	X
Methylene Chloride	X	X
1,1,1 Trichloroethane	X	X
Tetrachloroethylene	X	X
Toluene	X	X
Xylene	X	X
Methanol	X	X
Ethanol	X	X
Isopropyl Alcohol	X	X
Isobutanol	X	X
Butyl Acetate	X	X
Ethyl Acetate	X	X
Aliphatic Hydrocarbons	X	X
VOC Scan	X	X
Arsenic	X	
Barium	X	
Cadmium	X	
Chromium	X	
Lead	X	X
Mercury	X	

Table 1 Continued . . .

	<u>Groundwater</u>	<u>Soil</u>
Selenium	X	
Silver	X	
pH ✓	X	
TOC ✓	X	
TOX ✓	X	
Specific Conductivity	X	
% Solids		X

#### IV. TASK 3 - REPORT OF SITE INVESTIGATION

A thorough analysis and summary of all site investigations and their results will be prepared and presented in this section. The objective will be to ensure that the investigation data are sufficient in quality and quantity to support the corrective action study. The results and data from all site investigations will be organized and presented logically so that the relationship between site investigations for each medium are apparent.

The report will analyze all the field data gathered during this investigation and develop a summary of the type and extent of contamination at the site, including all significant pathways of contamination. An assessment will be included in the report in order to identify any potential or actual threats to public health, welfare and the environment.

Currently, there are no data which indicate that the site is posing any significant threat to public health, welfare or the environment. The assessment will further evaluate this situation to confirm that there are no threats.

The analysis of the site investigation will identify the objectives and alternative corrective actions which may be recommended to significantly mitigate the threat, if any, to public health, welfare or the environment.

If the investigation finds that contamination and/or an actual or potential threat to public health, welfare or the environment does not exist, then corrective actions will not be required and no further work will be conducted after completion of the Site Investigation Report.

The Site Investigation Report will include the following:

- a. Description of soil sampling procedures;
- b. Summary of soil laboratory test results;
- c. Copies of soil laboratory data sheets;
- d. Description of drilling and installation of wells;
- e. Copies of boring logs;
- f. Description of groundwater sampling procedure;
- g. Summary of groundwater test results;
- h. Copies of groundwater laboratory data sheets;
- i. Environmental Assessment; and
- j. Discussion of project objectives and alternative corrective action for evaluation in the corrective action study, if required.

## V. Task 4 - REVIEW OF ALTERNATIVE CORRECTIVE ACTIONS

The objective of the alternative corrective actions evaluation task is to evaluate alternative actions, if such action is required, on the basis of economic, environmental and engineering criteria, and to select the most cost-effective alternative or combination of alternatives for conceptual design and implementation. Should the site investigation determine corrective actions are not required, since no contamination or an actual or potential threat to public health, welfare or the environment exists at the site, then this and subsequent tasks will not be conducted.

### 4.1 - Initial Screening of Alternatives

An initial screening of the alternative corrective actions identified in Task 3 will be conducted. The objective of this subtask is to evaluate alternative corrective actions to eliminate alternatives clearly not feasible or appropriate based on cost, effects of alternative, and acceptable engineering practices. Alternatives that far exceed the costs of other alternatives evaluated and do not provide substantially greater public health or environmental benefit will be excluded from further consideration. Only those alternatives that effectively contribute to the protection of public health, welfare or the environment will be considered further. Alternatives must also be considered feasible, be applicable to the problem, and represent an acceptable means of addressing the problem.

### 4.2 - Detailed Analysis of Alternatives

The objective of this subtask is to develop engineering details on the remaining alternatives, perform an environmental assessment for each alternative, and prepare Order-of-Magnitude cost estimates. These

engineering details will include alternative descriptions and conceptual site layout drawings, operation and maintenance requirements, safety requirements and special engineering considerations. The environmental assessment will address each alternative in terms of the extent to which it is expected to effectively mitigate and minimize damage to, and provide adequate protection of public health, welfare and the environment, relative to the other alternatives analyzed. The cost estimates will include the total cost of implementing the alternative and the annual operating and maintenance costs.

Alternatives will be evaluated using technical, environmental and economic criteria. The areas that will be used to evaluate alternatives include: reliability; implementability; operation and maintenance requirements; environmental effects; safety requirements; and cost.

Evaluative considerations will be applied uniformly to each alternative. The lowest cost alternative that is technologically feasible and acceptable, and that adequately protects public health, wealth and the environment will be considered the cost-effective alternative.

#### 4.3 - Preliminary Report

A preliminary report will be submitted to the EPA that presents the results of the Alternative Corrective Actions Evaluation and the recommended alternative.

VI. TASK 5 - CONCEPTUAL DESIGN OF SELECTED ALTERNATIVE

The objective of the conceptual design task is to define the selected corrective action alternative for the design and implementation phases. The conceptual design will include an implementation schedule, phasing considerations, preliminary design criteria, preliminary site and facility layouts, operation and maintenance requirements, an outline of the health and safety plan, and a refined cost estimate. The conceptual design information will be included in the corrective action study report.

VII. TASK 6 - CORRECTIVE ACTION STUDY REPORT

The objective of the corrective action study report is to compile and describe the methods, results and conclusions of the alternative corrective actions evaluation task. The report will incorporate and include the following:

- a. Summary of the hazards and potential hazards, if any, for which corrective action is required;
- b. Detailed analysis of alternative technologies which can be employed to effectuate necessary corrective action;
- c. Description of all studies performed or evaluated to confirm the applicability of each alternative assessed;
- d. Unit cost estimates for each alternative;
- e. Operation and maintenance requirements with cost estimates for each alternative;
- f. Long-term integrity for each alternative;
- g. Timeliness of implementation for each alternative;
- h. A discussion of conformity to Federal, State and local laws and regulations, for each alternative; and
- i. Conceptual design and implementation schedule for the selected corrective action.



### VIII. IMPLEMENTATION SCHEDULE

The estimated time to complete each task of this project is presented in Table 2. Background information has been assembled, therefore Task 1 is complete at this time. The total time required to complete this project is 18 weeks. The schedule will be adjusted accordingly to include required review time by the EPA. In addition, this schedule may require revision, if the proposed site investigation work does not sufficiently define the extent of potential contamination and additional site work is necessary. This would extend the estimated time to complete Task 2. The project time schedule would be correspondingly adjusted.

HUKILL CHEMICAL CORPORATION  
BEDFORD, OHIO

TABLE 2

IMPLEMENTATION SCHEDULE

<u>Item</u>	<u>Estimated Completion Time (# of weeks)</u>
Task 1 - Background Information	*(1)
Task 2 - Site Investigation	6 <sup>(2)</sup>
Task 3 - Report of Site Investigation	3
Task 4 - Review of Alternative Corrective Actions	3
Task 5 - Conceptual Design of Selected Alternative	3
Task 6 - Corrective Action Study Report	<u>3</u>
Total:	18

Notes

1. Task 1 work has been completed.
2. Task 2 work may require additional time if the proposed site work does not sufficiently define the extent of potential contamination.

A PLAN AND IMPLEMENTATION SCHEDULE  
TO DETERMINE  
THE NATURE AND EXTENT OF CONTAMINATION  
THAT MAY HAVE RESULTED FROM OPERATIONS  
AT THE HUKILL CHEMICAL FACILITY

8-82

Prepared by

NUS Corporation  
910 Clopper Road  
Gaithersburg, Maryland 20878

Under Contract to

Hukill Chemical Corporation  
7013 Krick Road  
Bedford, Ohio 44146

August 23, 1982

Prepared by:



Donna Wallace  
Project Manager & Chief Hydrogeologist

Approved by:



J. T. Stone  
Vice President & General Manager  
Environmental Services Division

## TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	1-1
2 STUDY DESIGN	2-1
3 DATA COLLECTION PROGRAM	3-1
3.1 Monitoring Well Installation	3-1
3.2 Sample Collection and Analysis	3-4
3.3 Sampling Location Survey	3-12
4 DATA EVALUATION PROGRAM	4-1
4.1 Subsurface Conditions	4-1
4.2 Water Quality	4-2
4.3 Contamination Sources	4-6
5 RECOMMENDED ACTIONS	5-1
6 SCHEDULE	6-1
 <u>Figure</u>	
1 Groundwater Monitoring Well and Surface Water Sample Locations	3-2
2 Monitoring Well Construction	3-5
 <u>Table</u>	
1 Methods of Preservation	3-10
2 Volatile Organic Compounds	3-13
3 Analytical Techniques	3-14
4 EPA Drinking Water Standards	4-4
5 Implementation Schedule	6-2
6 Alternative Schedule	6-3
 <u>Form</u>	
1 NUS Well Record	3-3
2 Sampling Procedure Checklist	3-7
3 Sample Collection Information	3-9
4 Chain of Custody	3-11

## 1. INTRODUCTION

NUS Corporation (NUS) has designed the study presented here in response to a request from Hukill Chemical Corporation in Bedford, Ohio. The proposed study design is the result of NUS' best estimate of the effort needed to determine the nature and extent of contamination that may have resulted from the operation of the Hukill Chemical facility.

This study design was presented to the United States Environmental Protection Agency (EPA) in outline form on August 12, 1982 at a meeting in their offices in Chicago. Only two changes have been made in the study design since that time. Both changes were at the request of EPA. Additional permeability samples will be taken so that soil permeability can be determined for each distinguishable lithologic unit in each borehole. An alternate schedule has been added to facilitate EPA's determination of the value of samples collected after a rainfall.

## 2. STUDY DESIGN

The goal of the study, as designed, is to develop an implementation plan to reduce, if necessary, the offsite transport of pollutants resulting from the operation of the facility. The study includes data collection and evaluation to determine which pollutants handled by Hukill Chemical may be leaving the site, if Hukill Chemical's contribution can be considered significant, the remedial actions required, if any, and an evaluation of the effectiveness of those actions.

Two site visits were conducted by an NUS hydrogeologist to determine the best study design to accommodate the need for early results based on sound geologic and hydrologic data. Many approaches were considered before the plan of action, presented here, was selected. One of these alternative approaches included detailed chemical soil analyses, but this approach was rejected because of the non-reproducibility of such analyses and as a result of preliminary estimations of the extent of possible contamination. Instead, it was determined that the data collection effort should be directed toward the evaluation of the offsite migration of contaminants. This approach was based on the desire to reduce offsite contamination, rather than to characterize the onsite distribution of contaminants. The basic premise of the study design is the evaluation of contaminants moving within the unconsolidated materials to areas off the Hukill Chemical property and, therefore, posing a potential threat. Movement of these contaminants is either through solution and transportation by groundwater or through adsorption and erosion of soil to surface water. For these reasons, a detailed water sampling and analysis program has been developed.

Surface water quality will be evaluated to determine the facility's impact. Three sampling sites have been selected to provide the basis for examining the surface water quality entering the site, the effect of the discharge from outfall 001, and the quality of groundwater runoff to the stream. Groundwater runoff is used here to indicate the precipitation that percolates downward, travels through the unconsolidated deposits and is discharged to the stream.

Based on the regional geology, confined rock aquifers are expected to be greater than 100 feet below the land surface. If these aquifers are contaminated, it is probably the result of activities in the recharge area, rather than activities at the Hukill Chemical plant.

Onsite soil borings suggest that the shale bedrock underlying the site occurs approximately 15 to 20 feet below the surface in the area near the north tank farm and dips up to one foot in ten to the north-northeast of the site. The upper portions of the bedrock consist of weathered shale and are overlain by glacial till and site fill. The permeability of the glacial till was measured in the laboratory at  $K = 8.6 \times 10^{-8}$ ,  $2.8 \times 10^{-5}$ , and  $2.2 \times 10^{-8}$  centimeters per second in three different nearby borings. The glacial till is typical of the area with silty and clayey deposits in close proximity. Rainfall in the area percolates through the soil and weathered shale until it encounters the tight shale bedrock. It then migrates down-dip and is discharged at the point a stream channel intersects its path.

Groundwater moving through the unconsolidated deposits will be sampled directly above the shale bedrock. Since this groundwater zone is a localized phenomenon, it is impossible to predict flows. The groundwater flow rate may be such that the discharge (not groundwater runoff) to surface water is slow and, therefore, the consolidated deposits will contain a constant flow. Conversely, the groundwater flow rate may be fairly high through the weathered shale and, therefore, discharge to surface water may be rapid. If the latter is the case, sufficient groundwater for sampling will only be available after a significant rainfall event. This situation does not affect the study design, only the sampling period.

The monitoring well locations have been carefully selected to provide a wide range of information. The upgradient well is located in a manner to facilitate the determination of groundwater quality that is not effected by facility operation and to offer reasonably representative information concerning the groundwater effects of upgradient offsite operations. Two downgradient wells are located at points designed to provide sufficient information to determine flow direction and to provide information to be used in evaluating whether the onsite problems are the result of specific units or the result of past opera-

tions in general. The last well has been located near the buried cistern, since it has been anticipated that contamination resulting from this area may mask the other sources of contamination.

Optimally, water samples should be collected during both dry and wet periods, since high water tables may be removing additional contaminants from the soil. Unfortunately, if recommended remedial measures are to be implemented before winter, sampling must proceed as rapidly as possible.

Once the initial data is collected and evaluated, NUS will prepare recommendations for additional actions on the part of Hukill Chemical. An interim report, containing the study findings and recommendations will be submitted to Hukill Chemical and the EPA. Following discussions with the EPA, NUS will prepare an implementation plan for the agreed-upon action. This plan will also contain a program to measure the effectiveness of the actions and an ongoing monitoring program, if deemed necessary.



### 3. DATA COLLECTION PROGRAM

The data collection program will consist of installing groundwater monitoring wells, collecting and analyzing groundwater and surface-water samples, and surveying the sample collection points. The first phase of the program will provide information concerning the subsurface materials at the site collected during the drilling and logging of the boreholes for well installation. The well records will also provide the information necessary to prepare geologic cross-sections of the materials beneath the site. Water levels measured during sample collection (second phase) combined with the results of the survey (third phase) will provide the information for the construction of groundwater flow diagrams. These diagrams, plus the soil permeability tests, will provide the data to be used to estimate groundwater flow rates.

The field procedures for data collection are discussed in detail below.

#### 3.1 Monitoring Well Installation

A hydrogeologist from NUS will site four monitoring wells at the Hukill Chemical facility. Groundwater flow in the unconsolidated deposits is assumed to be in the direction of the onsite stream and approximately north to northeast. The wells will be located in the general areas indicated on Figure 1. Well number G-1 is assumed to be the upgradient well and wells number G-2 and G-3 the downgradient wells for the facility. Well number G-2 will be located in the vicinity of the downgradient end of the easterly erosion channel. Well number G-3 will be located downgradient of the north tank farm. Well number G-4 will be located nearby and downgradient from the buried cistern. All wells will be sited in areas accessible to drilling equipment. Since the site is nearly flat (surficial topography), the two most northerly downgradient wells (G-2 and G-3) will be installed first to aid in more precisely locating the upgradient well (G-1, to be installed last).

The drill rig and operators will be supplied by a local drilling firm. Donna Wallace, a hydrogeologist from NUS, will log the boreholes through visual

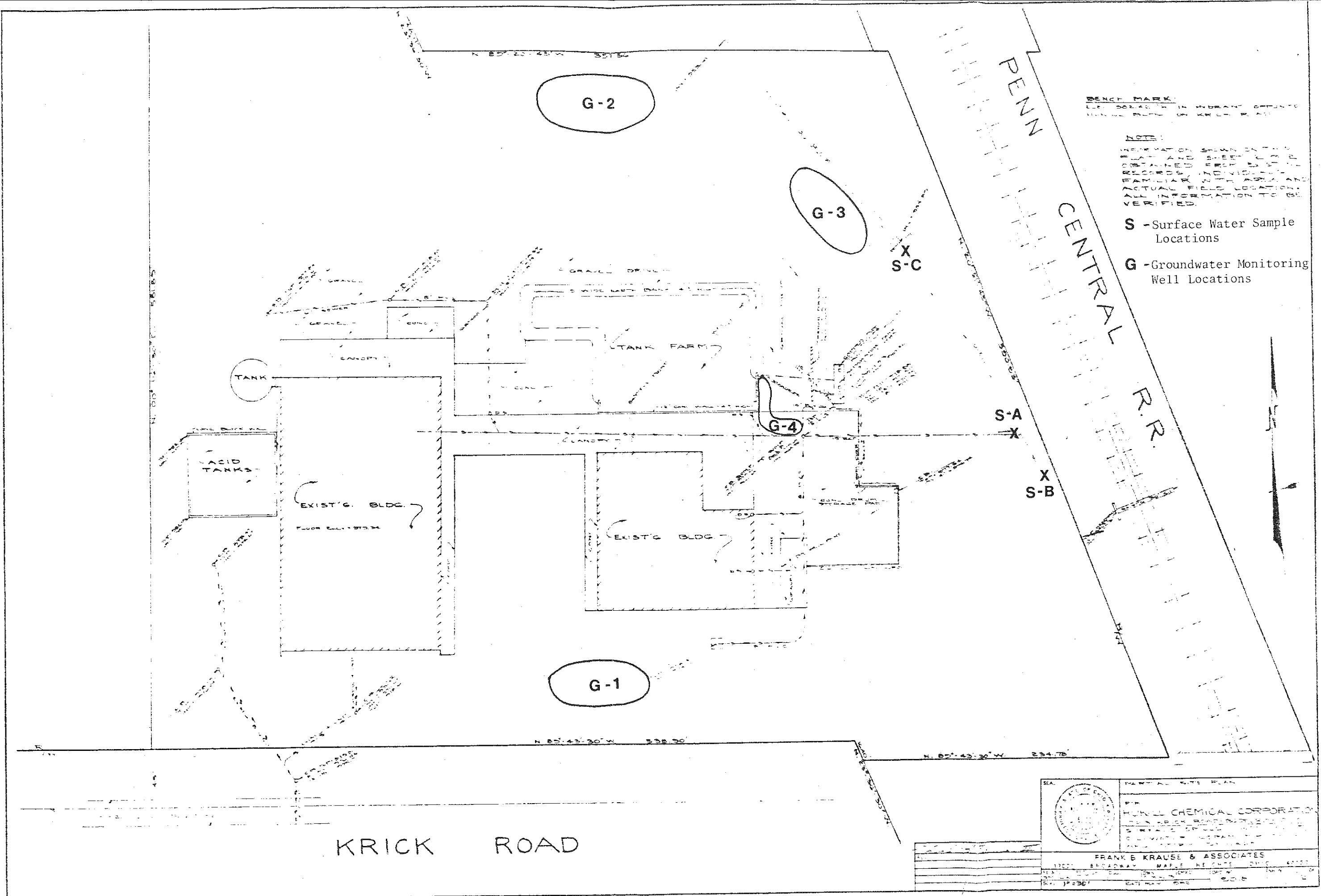


Figure 1. GROUNDWATER MONITORING WELL AND SURFACE WATER SAMPLE LOCATIONS

FORM 1  
NUS WELL RECORD

Project: \_\_\_\_\_  
Well No.: \_\_\_\_\_  
Coordinates: \_\_\_\_\_  
On-Site Geologist: \_\_\_\_\_  
Elevation (top of pipe): \_\_\_\_\_  
Elevation (land surface): \_\_\_\_\_  
Elevation (water table): \_\_\_\_\_  
Date Measured: \_\_\_\_\_  
Status of Well: \_\_\_\_\_

CASING

Type: \_\_\_\_\_  
Diameter: \_\_\_\_\_  
Length: \_\_\_\_\_  
Type of Joint: \_\_\_\_\_  
Screen Slot: \_\_\_\_\_  
Screen Length: \_\_\_\_\_  
Screen Setting: \_\_\_\_\_

## DRILLING

Drilling Started: \_\_\_\_\_  
 Drilling Completed: \_\_\_\_\_  
 Drilling Company: \_\_\_\_\_  
 Registration No.: \_\_\_\_\_  
 Permit No.: \_\_\_\_\_  
 Name of Driller: \_\_\_\_\_  
 Type of Rig: \_\_\_\_\_  
 Drilling Fluid: \_\_\_\_\_

GRAVEL

Type: \_\_\_\_\_  
Size: \_\_\_\_\_  
Volume: \_\_\_\_\_  
Depth: \_\_\_\_\_

## HOLE DATA

Hole Diameter: \_\_\_\_\_  
 Thickness of Overburden: \_\_\_\_\_  
 Depth Drilled in Rock: \_\_\_\_\_  
 Total Depth of Hole: \_\_\_\_\_

GROUT

Type: \_\_\_\_\_  
 Method: \_\_\_\_\_  
 Volume: \_\_\_\_\_  
 Depth: \_\_\_\_\_

## DEVELOPMENT

Method: \_\_\_\_\_  
Rate of Flow: \_\_\_\_\_  
Length of Time: \_\_\_\_\_

Type: BACKFILL

## COMMENTS

*(continued)*

# DRILLING LOG

From Depth To

<u>Formation</u>	<u>Description</u>
100	100

5

inspection of the materials removed (see Form 1) and will supervise the installation of the monitoring wells. Permeability samples will be taken at each distinguishable change in lithology. All boreholes will be augered to the top of the shale bedrock (through the weathered shale, which is considered to be the uppermost water-producing zone).

Monitoring-well installation will consist of inserting 2-inch industrial-grade (type 304), schedule 5 (0.065-inch thick) stainless steel casing (see Figure 2). All joints will consist of flush threads welded to the pipe and wrapped with teflon tape. Each well will be screened for the lower 10 feet with seven slot (0.007-inch) screen. Screens will be capped at the bottom. Each well will be gravel packed for a minimum of 2 feet above the screen with clean, inert, and insoluble aggregate. The annular space will be backfilled to the surface with bentonite. A 3-foot cement collar will be placed at the top of the borehole to hold the well securely in place and to direct run-off away from the casing. The top of the casing will be fitted with a locking cap.

If sufficient water is available for sampling at the time of well installation, these samples will be collected as described later. Once the samples are collected, the wells will be developed by surging with potable water to clear the screens for future sampling. Since development affects water quality only by dilution of the existing contaminants, well development after sample collection will not affect the representative nature of the samples. If sufficient water is not available to sample wells immediately, then samples will not be taken until a significant rainfall event has occurred. The addition of potable water during development will not impact the concentration of pollutants at that time, since the rainfall will have already provided dilution.

### 3.2 Sample Collection and Analysis

The sample collection points were indicated on Figure 1 and are described as follows:

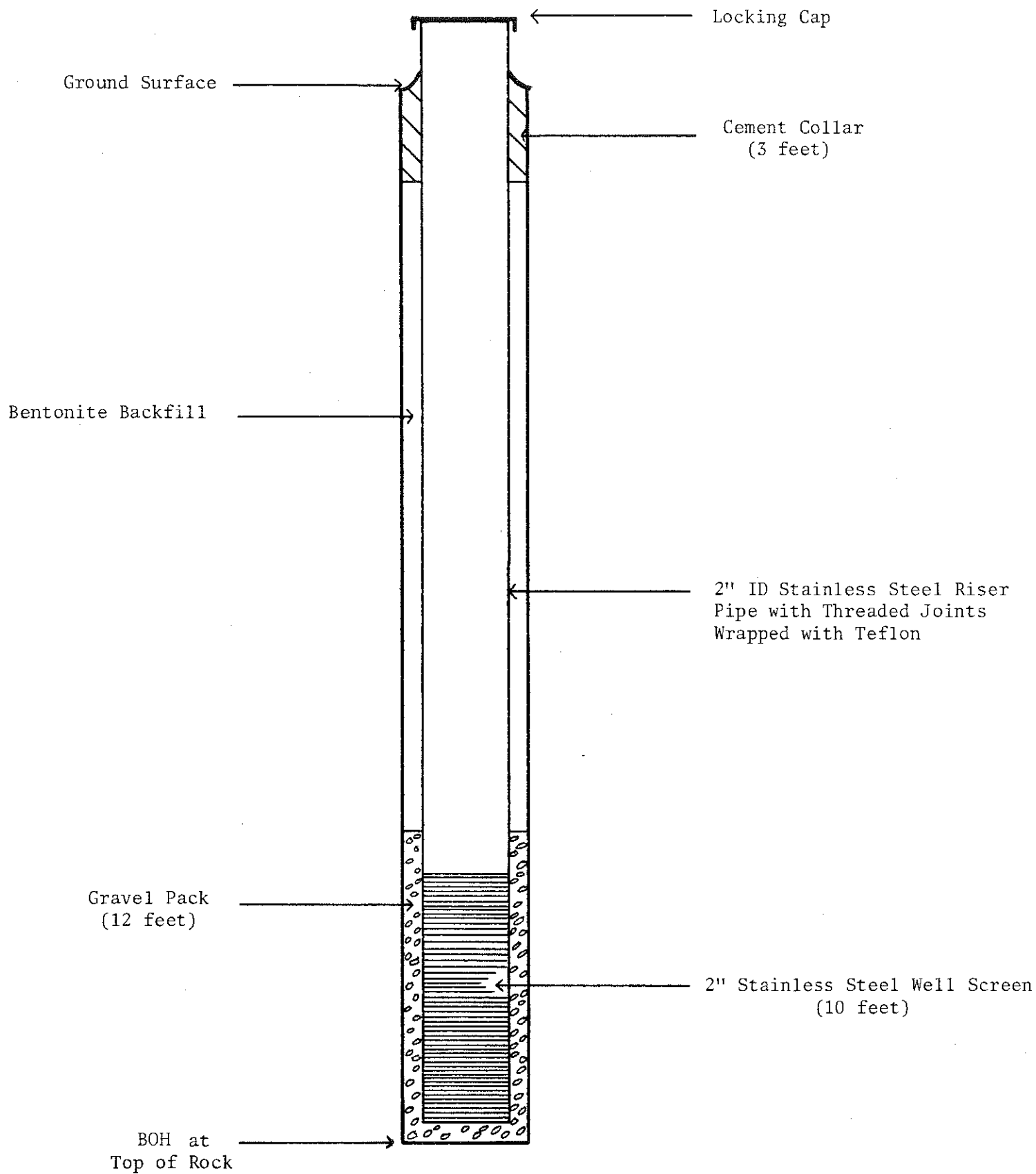


Figure 2 MONITORING WELL CONSTRUCTION

- S-A. Discharge from Outfall 001
- S-B. Surface water above Outfall 001
- S-C. Surface water as it enters the culvert (downstream of Outfall 001)
- G-1. Groundwater upgradient of Hukill operations
- G-2. Groundwater at the downgradient end of the easterly erosion channel
- G-3. Groundwater downgradient from the north tank farm
- G-4. Groundwater near (downgradient) the buried cistern.

Samples will be collected from each of the above sampling points immediately after well installation if sufficient water is available. If not, all samples will be collected as soon as possible (estimated to be within 24 hours) after the first significant rainfall event. Sample collection will be performed by a qualified chemist from the Wadsworth Testing Laboratories, in conformance with the procedures described below.

Sample collection procedures are considered to be the most significant step in the sampling and analysis program. It is important that the correct methods be used and that consistency be maintained throughout the life of the sampling program. Therefore, a detailed "Sampling Procedure Checklist" (see Form 2) will be used each time samples are collected. The field data will be recorded on a "Sample Collection Information" sheet (see Form 3), which will be filed with the analytical results.

Sample preservation will be in accordance with "Methods for Chemical Analysis of Water and Wastes" (1974), USEPA 625/6-74-003, as described in Table 1. All samples will be iced and delivered to the laboratory for analysis.

Chain of custody control will be maintained throughout the sampling and analysis program. The sample collector will initiate the chain of custody record (see Form 4) when the well is sampled. This record will travel with the

sample bottles to the laboratory. Sample bottles will be sealed prior to shipment and the condition of the seal will be inspected prior to analysis and

FORM 2  
SAMPLING PROCEDURE CHECKLIST

- \_\_\_\_\_ 1. Before going in the field, fill in the following information on the "Sample Collection Information" form:

Sample Collector  
Sample Source (Well Number or Surface Water Location Letter)  
Air Temperature  
Date Collected  
Reason for Sampling  
Depth of Well (from top of pipe).

- \_\_\_\_\_ 2. Assemble the following equipment:

Pump or Bailer and Measuring Bucket  
Watch  
Pocket Calculator  
Measuring Tape  
Thermometer  
Filtration Apparatus  
Sample Bottle  
pH Meter  
Ice Chest and Ice  
Distilled Water  
Sample Collection Information Sheets  
Chain of Custody Forms.

- \_\_\_\_\_ 3. Proceed to first well and record the time.

- \_\_\_\_\_ 4. Measure the water level and record the depth to the top of the water surface.

- \_\_\_\_\_ 5. Determine the submerged casing volume (standing water volume) in the well from the following equation:

$$V = \pi r^2 h$$

where V = volume  
r = radius of the casing  
h = standing water height.

- \_\_\_\_\_ 6. Using the pump or bailer, remove three casing volumes of water from the well. Record the volume of water removed. If the well is not able to recharge at a rate sufficient to evacuate three well casing volumes, the well should be pumped or bailed dry.

- \_\_\_\_\_ 7. Measure and record the depth to water again. If the second depth to water is significantly less than the first, the well should be allowed to recharge.

- \_\_\_\_\_ 8. Measure the sample pH of four samples and record.
- \_\_\_\_\_ 9. Fill all pretreated sample bottles. Filter the samples if turbid; remove and discard the sediment. Record the sample temperature at the time of withdrawal and the sample appearance.
- \_\_\_\_\_ 10. Seal the sample bottles with labels. Labels should contain sample number, date, and name of collector.
- \_\_\_\_\_ 11. Transfer all sample bottles to ice chest and pack with ice.
- \_\_\_\_\_ 12. Clean all equipment by rinsing thoroughly with distilled water and proceed to the next well.
- \_\_\_\_\_ 13. Begin collecting surface water samples. Estimate the flow and record.
- \_\_\_\_\_ 14. Repeat steps 8 through 11 while sampling the surface water and outfall 001.
- \_\_\_\_\_ 15. Transport all samples to the laboratory for analysis.



FORM 3  
SAMPLE COLLECTION INFORMATION

Site: \_\_\_\_\_  
Address: \_\_\_\_\_  
Sample Collector: \_\_\_\_\_ Firm: \_\_\_\_\_  
Sample Type: \_\_\_\_\_ Sample Source: \_\_\_\_\_  
Lab Sample No.: \_\_\_\_\_ Air Temperature: \_\_\_\_\_  
Date Collected: \_\_\_\_\_ Time Collected: \_\_\_\_\_  
Reason for Sampling: \_\_\_\_\_

Water Level Information (from top of pipe)

Depth to Water before Purging: \_\_\_\_\_ Depth of Well: \_\_\_\_\_  
Depth to Water after Purging: \_\_\_\_\_ Volume Removed: \_\_\_\_\_

Surface Water Information

Estimated Flow: \_\_\_\_\_ Method: \_\_\_\_\_

Field Testing

Sample Appearance: \_\_\_\_\_  
\_\_\_\_\_  
Color: \_\_\_\_\_ Clarity: \_\_\_\_\_  
Sample Temperature: \_\_\_\_\_ Time Iced: \_\_\_\_\_  
Sample pH: \_\_\_\_\_ Sample pH: \_\_\_\_\_ Sample pH: \_\_\_\_\_  
Samples Filtered: \_\_\_\_\_  
\_\_\_\_\_

Sample Shipment

Where Shipped: \_\_\_\_\_  
\_\_\_\_\_  
Method of Shipment: \_\_\_\_\_ Chain of Custody Needed: \_\_\_\_\_

Comments:

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

TABLE 1  
METHODS OF PRESERVATION

Parameter	Preservation Method (1)	Maximum Holding Time (2)
pH	Cool to 4°C	6 hours (on-site)
Total Organic Carbon	Add H <sub>2</sub> SO <sub>4</sub> to pH < 2; Cool to 4°C	24 hours
Chemical Oxygen Demand (O <sub>2</sub> )	Add H <sub>2</sub> SO <sub>4</sub> to pH < 2	7 days
Chloride	Cool to 4°C (None required)	28 days
Arsenic	Add 6 ml conc. HNO <sub>3</sub> /l	6 months
Barium	Filter; Add 5 ml conc. HNO <sub>3</sub> /l	6 months
Cadium	Filter; Add 5 ml conc. HNO <sub>3</sub> /l	6 months
Chromium	Filter; Add 5 ml conc. HNO <sub>3</sub> /l	6 months
Lead	Filter; Add 5 ml conc. HNO <sub>3</sub> /l	6 months
Mercury	Filter; Add 5 ml conc. HNO <sub>3</sub> /l	38 days
Selenium	Add 5 ml conc. HNO <sub>3</sub> /l	6 months
Silver	Filter; Add 5 ml conc. HNO <sub>3</sub> /l	6 months
Volatile Organics	Cool 4°C	14 days

(1) Methods for Chemical Analysis of Water and Wastes (1979), EPA 600/4-79-020.

(2) Methods for Chemical Analysis of Water and Wastes (1974), USEPA 625/6-74-003.

FORM 4  
CHAIN OF CUSTODY

Site Sampled: \_\_\_\_\_

Address: \_\_\_\_\_

Sample Collector: \_\_\_\_\_ Phone: (    ) \_\_\_\_\_

Sample Shipper: \_\_\_\_\_ Phone: (    ) \_\_\_\_\_

Sample Type: \_\_\_\_\_ Sample Source: \_\_\_\_\_

Date Collected: \_\_\_\_\_ Time Collected: \_\_\_\_\_

Receiving Laboratory: \_\_\_\_\_

Address: \_\_\_\_\_

Condition of Sample: \_\_\_\_\_

Seal Intact?: \_\_\_\_\_ Sample Temperature: \_\_\_\_\_

Date Received: \_\_\_\_\_ Time Received: \_\_\_\_\_

Chain of Possession:

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Title

\_\_\_\_\_  
Date & time of receipt/initials

\_\_\_\_\_  
Date & time of release/initials

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Title

\_\_\_\_\_  
Date & time of receipt/initials

\_\_\_\_\_  
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Signature

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Title

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Date & time of release/initials

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Title

\_\_\_\_\_  
Date & time of receipt/initials

\_\_\_\_\_  
Date & time of release/initials

noted on the chain of custody record. Once analysis is completed, the record will be placed in company files.

The inorganic chemical analyses to be performed have been shown in Table 1. The organic analyses will consist of a qualitative scan to identify the specific organic compounds shown in Table 2. A quantitative analysis will be performed on up to five parameters, per sample, found in the greatest concentrations.

The chemical analyses required will be performed in accordance with EPA methods contained in "Methods for Chemical Analysis of Water and Wastes" (1979), EPA 600/4-79-020, and "Microbiological Methods for Monitoring the Environment, Water and Wastes" (1978), EPA 600/8-78-017. The preservative and holding time requirements set forth in the 1974 edition of the same manual were shown in Table 1. Brief descriptions of the methodology are shown in Table 3.

### 3.3 Sampling Location Survey

All seven sampling points will be surveyed for both horizontal and vertical control. Elevations will be shot on the top of the casing and the distance to the ground-surface will be measured. The hydrant on Krick Road opposite the Hukill buildings will serve as the bench mark (elevation 982.42). Survey work will be performed by Frank B. Krause and Associates of Maple Heights, Ohio (who have done previous onsite survey work).

TABLE 2  
VOLATILE ORGANIC POLLUTANTS

---

EPA Priority Pollutants	• Acrolein
	• Acrylonitrile
	• Benzene
	• Bis (Chloromethyl) Ether
	• Bromoform
	• Carbon Tetrachloride
	• Chlorobenzene
	• Chlorodibromomethane
	• Chloroethane
	• 2-Chloroethylvinyl Ether
	• Chloroform
	• Dichlorobromoethane
	• Dichlorodifluoromethane
	• 1,1-Dichloroethane
	• 1,2-Dichloroethane
	• 1,1-Dichloroethylene
	• 1,2-Dichloropropane
	• 1,2-Dichloropropylene
	• Ethylbenzene
	• Methyl Bromide
	• Methyl Chloride
	• Methylene Chloride
	• 1,1,2,2-Tetrachloroethane
	• Tetrachloroethylene
	• Toluene
	• 1,2-Trans-Dichloroethylene
	• 1,1,1-Trichloroethane
	• 1,1,2-Trichloroethane
	• Trichloroethylene
	• Trichlorofluoromethane
	• Vinyl Chloride

---

Hukill Chemical RCRA Waste Analysis Plan	• Methylene Chloride ✓
	• Toluene ✓
	• 1,1,1-Trichloroethane ✓
	• Trichloroethylene
	• Xylene ✓
	• N-Butyl Acetate ✓
	• Ethyl Acetate ✓
	• Methyl Ethyl Ketone ✓
	• Di-isobutyl Ketone
	• Acetone ✓
	• Cellulosolue Acetate
	• Methanol ✓
	• Ethanol ✓
	• Propanol

---

TABLE 3  
ANALYTICAL TECHNIQUES

Parameter	Methodology
Chemical Oxygen Demand	Digestion with standard sodium dichromate solution, titration with standard ferrous ammonium sulfate solution to ferrous endpoint.
Total Dissolved Organic Carbon	Nondispersive infrared spectrometric measurement of carbon dioxide after conversion in high temperature furnace. Sample is prefiltered on 0.45 $\mu$ m membrane filter.
pH	Electrometric determination with glass and calomel electrodes. Calibration by means of appropriate standard buffer solutions.
Chloride	Electrometric determination with selective ion electrode, calibration with standard solutions.
Heavy Metals (excluding arsenic, mercury, and selenium)	Atomic absorption spectrometry (AAS) using direct aspiration. Calibration by multiple standards spiked into sample to eliminate sample-matrix effects.
Arsenic	AAS using hydride vapor method.
Mercury	AAS using cold vapor method.
Selenium	AAS using hydride vapor method.
Volatile Organics (VOA)	Purge and trap GC/MS.

#### 4. DATA EVALUATION PROGRAM

The data evaluation program will consist of three components. First, the subsurface conditions beneath the facility will be described in detail, including geologic cross-sections and groundwater flow diagrams.

Second, the water quality data will be subjected to a detailed evaluation to determine which pollutants, and the associated concentrations, are being transported offsite at the Hukill Chemical facility. This evaluation will provide a description of the nature of contamination. The extent of contamination will be determined by the concentrations of pollutants contributed by Hukill Chemical. These concentrations will be calculated by subtracting the concentrations entering the site from those leaving the site. The significance of each pollutant and the resulting concentrations will be evaluated in as much detail as possible.

Finally, the probable sources of contamination will be examined. The offsite contributions will be quantified as those concentrations entering the facility and the evaluation of the significance of the Hukill Chemical contribution will be based on these levels of offsite contribution. Where the Hukill Chemical contribution appears significant, probable onsite sources will be identified based on the data evaluation.

Each of these components is discussed in more detail below.

##### 4.1 Subsurface Conditions

The subsurface materials beneath the Hukill Chemical site will be described from the well records prepared by NUS. Each distinguishable unconsolidated deposit and the weathered shale will be described and the results of the permeability tests reported. Geologic cross-sections will be prepared for two

areas--between boreholes G-1 and G-2 and between boreholes G-1 and G-3 through G-4.

The groundwater levels measured when samples are collected, combined with the surveyed well control, will be used to construct groundwater flow diagrams. These diagrams will indicate flow direction and will be of sufficient detail to determine the slope of the water table at the time of sampling. If groundwater samples are collected after a rainfall, in addition to other samples, a second flow diagram will be prepared.

Groundwater flow rates will be estimated using Darcy's Law and literature values for porosity. Permeability will be determined from the soil test data and gradients will be calculated from the groundwater flow diagrams.

#### 4.2 Water Quality

The water quality data will be assembled in two tables--one for groundwater quality and one for surface water quality plus outfall 001. An interpretive table will also be prepared. The groundwater concentrations entering the site (G-1) will be subtracted from the concentrations leaving the site (the mean of G-2 and G-3). These concentrations will be considered as the groundwater contribution resulting from the operation of Hukill Chemical. The groundwater runoff contribution to the stream will also be determined. This calculation will be the result of subtracting the concentrations in outfall 001 and the concentrations in the upstream sample (S-B) from the concentrations in the downstream sample (S-C). These two calculations will be tabulated with the Outfall 001 concentrations and the concentrations near the buried cistern. Therefore, this interpretive table will delineate the concentrations resulting from groundwater, the groundwater runoff, Outfall 001, and the buried cistern.



Once this table has been constructed, individual concentrations of specific parameters will be evaluated, to the extent possible, to determine the significance of the contribution by Hukill Chemical. This evaluation will be conducted as two elements, the inorganic parameters and the organic parameters.

The priority heavy metal (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) concentrations, chloride, and pH will be compared to the EPA drinking water standards shown in Table 4. This comparison will provide the basis for an evaluation of the significance of the concentrations found for the inorganic parameters.

The organic compounds are expected to pose a more difficult problem, since very little is known about the environmental effects of most organics. Therefore, the significance of the organic contribution will be evaluated through a statistical comparison of total organic carbon concentrations entering and leaving the site. A similar comparison will be performed for pH.

Comparisons of the upgradient and downgradient water quality will be performed statistically, based on the Students' t-test at the 0.01 level of significance. A one-tailed test will be used for the evaluation of changes in total organic carbon (TOC), since only increases over the upgradient quality are significant. For pH, a two-tailed test will be used since both increases and decreases are significant.

Specifically, the four values of TOC concentrations found at the upstream surface water sampling point (S-B) will be used to calculate the background mean and variance. The mean and variance of the four concentrations for TOC found at the downstream surface water sampling point (S-C) will be compared to the background values. A Students' t-test will be performed and a t-value calculated. If the calculated value for TOC is larger than the table value

TABLE 4  
EPA DRINKING WATER STANDARDS

Parameter	Maximum Contaminant Level (mg/L)
pH	6.5 - 8.5 *
Chloride	250*
Arsenic	0.05
Barium	1.0
Cadmium	0.01
Chromium	0.05
Lead	0.05
Mercury	0.002
Selenium	0.01
Silver	0.05

\* These are secondary EPA standards (40 CFR 143). The remaining standards (40 CFR 141) shown are primary (health related).

(3.143, assuming 6 degrees of freedom), then the change in TOC will be considered significant. If the calculated value is negative for pH, the absolute value will be used, since increases or decreases are significant. This absolute value will be compared to the table value (3.707).

It should be recognized that pH does not lend itself well to comparison statistics since it is not a linear function. That is, a decrease in pH from 6.5 to 6.0 is not the same amount of change as an increase from 8.5 to 9.0, since pH is logarithmic. However, statistical comparisons of TOC may not be conclusive by themselves and so pH will also be examined. Similar comparisons for TOC and pH will be performed to compare the upgradient groundwater (G-1) to the mean concentrations of the downgradient groundwater at G-2 and at G-3.

If a significant difference is found between the TOC concentrations upstream and downstream, then the Students' t-test will be used to evaluate the influence of outfall 001. The TOC concentrations in outfall 001 (S-A) will be compared to the concentrations found in the downstream surface water (S-C). If these differences are statistically significant, it will be assumed that there is a significant groundwater runoff contribution to surface water at the facility.

If a significant difference is found in the comparisons of groundwater quality, then the TOC concentrations from the groundwater near the buried cistern (G-4) will be compared to downgradient groundwater quality (the mean of G-2 and G-3). If no statistically significant difference can be established between the downgradient groundwater concentrations of TOC and the groundwater concentrations of TOC near the buried cistern, it will be concluded that the majority of the organic contamination that is being measured in the water is resulting from the buried cistern.

Where appropriate, the concentrations of specific organic compounds contributed by Hukill Chemical will also be compared to the draft Suggested No Adverse Response Levels (SNARLS) recommended by EPA's drinking water office. It is not expected that the SNARLS will be very useful, however, since they were designed for spills affecting drinking water sources. However, the SNARLS may help to provide an order-of-magnitude comparison if one examines the allowable concentrations for 1-day exposures versus the concentrations for 10-day exposures in drinking water. That is, 1-day exposure concentrations are often nearly 10 times the 10-day exposure concentrations in drinking water. Therefore, if the water is not consumed, the concentrations allowable should be orders of magnitude higher than even the 1-day concentrations.

#### 4.3 Contamination Sources

A table will be prepared to describe the relative contribution of onsite and offsite sources to offsite contamination. This table will show the percentage of contribution by these two sources for each parameter measured. Groundwater and surface water will be considered separately. The inorganic parameters where the concentrations being transported offsite (S-C and G-2 and G-3) are below the drinking water standards, will be eliminated from further consideration. The organic parameters found in concentrations below the detection limits will also be eliminated. Additional organic parameters will be eliminated if it can be demonstrated through the use of the SNARLS that the levels are acceptably low. The parameters remaining will be evaluated as described below.

Where Hukill Chemical contributions of specific groundwater contaminants are high, the concentrations in the groundwater near the buried cistern will be considered first. If specific concentrations cannot be accounted for near the buried cistern (G-4), downgradient well (G-2 and G-3) analyses will be

examined. A similar procedure will be used for specific surface water contaminants and outfall 001 will be examined first.

Finally, the probable onsite sources will be identified and described.

## 5. RECOMMENDED ACTIONS

The results of the evaluations conducted under Section 4 will be used to determine the recommended actions at the site. These actions will be designed to reduce the offsite transport of pollutants resulting from the operation of the Hukill Chemical plant. The collected data, the results of the data evaluations, and the recommended actions will be presented in an interim report. This report will be submitted concurrently to Hukill Chemical Corporation and the EPA. A meeting will be scheduled to discuss the findings and to determine which remedial actions, if any, are to be performed at the facility.

NUS will prepare an implementation plan based on the results of this meeting. The plan will contain a discussion of the remedial action to be performed (including all the information to carry out that action), the monitoring program necessary to determine the effectiveness of the action, and an implementation schedule. This plan will be submitted to EPA for approval before the remedial action is initiated.

## 6. SCHEDULE

An important limiting factor in the design of the data collection program was the desire on the part of Hukill Chemical to proceed with the remedial action program, if necessary, before winter. Although NUS seldom recommends that "single-point-in-time" water quality analyses be used to evaluate existing conditions, no other alternative appears feasible within the available time. This schedule assumes that the monitoring wells can be installed without using water or drilling additives and that sufficient water will be available in the completed wells to allow for immediate sampling.

Hukill Chemical and their geotechnical contractor, NUS, are committed to the schedule presented in Table 5. This schedule presumes that EPA approval will be secured by the end of August and that sufficient groundwater in the unconsolidated deposits will be available for sampling at the time of well installation. If sufficient water is not available, the EPA will be notified by phone, followed by a letter, that the schedule presented in Table 6 will be implemented.

The significance of the alternative schedule presented in Table 6 is that it cannot be predicted when sufficient rainfall will occur to allow for sample collection. It can be assumed that if the groundwater flow rate is high enough to prohibit groundwater sampling during dry periods, then it should allow for sampling shortly after rainfall. However, the occurrence of rainfall in September cannot be predicted.

The schedule shown in Table 6 indicates two phases of data collection. If samples cannot be collected until after a rainfall, the first phase will include well installation only. If two sets of samples are collected, water quality analyses will be conducted after each data collection phase. Slightly more time has been allowed for laboratory analyses under the alternative schedule, since it may not be possible to secure commitments at the later

TABLE 5  
IMPLEMENTATION SCHEDULE

● Meet with USEPA	August 12
● Submit Approvable Plan to USEPA	August 23
● Meet with USEPA to Secure Approval	August 30
● Complete First Phase Data Collection	September 17
● Receive Laboratory Results	October 1
● Complete First Phase Data Evaluation and Submit Interim Report to USEPA	October 18
● Meet with USEPA to Discuss Remedial Action	October 28



TABLE 6  
ALTERNATE SCHEDULE

• Meet with USEPA	August 12
• Submit Approvable Plan to USEPA	August 23
• Meet with USEPA to Secure Approval	August 30
• Complete First Phase Data Collection	September 17
• Complete Second Phase Data Collection	Unknown
• Receive Laboratory Results of Second Phase Data	3 Weeks After Data Collection
• Complete Data Evaluation and Submit Interim Report to USEPA	4 Weeks After Receipt of Lab Results
• Meet with USEPA to Discuss Remedial Action	10 Days After Submittal of Interim Report

date. The data evaluation and preparation of the interim report includes additional time, since additional data will be evaluated. If only one set of data is collected, then the evaluation period can be limited to three weeks.